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CASE STUDIES OF HAZARDOUS WASTE TREATMENT TO REMOVE VOLATILE ORGANICS: VOLUME I

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Case studies are presented for treatment of refinery wastes in a pilot-scale thin-film evaporator, the removal of volatiles from industrial wastewater for two steam strippers, and the removal of semivolatiles from water by steam stripping followed by liquid-phase carbon adsorption. This report provides data on removal efficiency, air emissions, process residuals, treatment costs, and process limitations. Details on sampling and analytical procedures, quality assurance, and process data are contained in the Appendixes (Volume II).

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small and businesses in handling their wastes responsibly and economically.

This report presents the results of field assessments of three waste treatment techniques that have the potential for use in control of emissions of volatile organic compounds from hazardous waste facilities by removing those compounds from the waste streams. Those treatment techniques are thin-film evaporation, steam stripping, and steam stripping with carbon adsorption. The report is intended for use by government agencies which are considering ways to reduce emissions from hazardous waste facilities and by facility operators and managers who wish to do the same. For additional information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Three treatment processes were investigated for the removal of volatile organic (VO) compounds from hazardous waste: thin-film evaporation, steam stripping, and steam stripping with carbon adsorption. The data collected included the VO removal effectiveness, air emissions from the process, cost, and process limitations.

The thin-film evaporator (TFE) study was a pilot-scale evaluation of the TFE for removal of VO from petroleum refinery wastes. The study was performed under different controlled conditions at three temperatures, three flow rates, and under both vacuum and atmospheric pressure. The removal of volatile compounds was greater than 99 percent, and the removal of semivolatiles ranged from 10 to 75 percent depending upon the processing conditions. When the system was operated under vacuum, some carryover of the feed resulted in a condensate that was a milky-white emulsion, which would require additional treatment to separate the oils and water. Vent rates from the condenser were found to depend on the type of waste and the quantity of light hydrocarbons, which are difficult to condense. The cost estimates for the TFE plus land treatment of the residuals yielded costs that were comparable to or less than the cost of land treating the original waste without pretreatment to remove VO.

Two full-scale steam strippers used to treat industrial wastewater containing about 6,000 ppm of purgeable VO were tested. The tray column stripper processed about 850 L/min of water that contained primarily ethylene dichloride and chloroform. Total VO removal averaged about 99.8 percent with an average concentration of 9.7 ppm in the bottoms. The condenser removed about 99 percent of the VO from the vapor and yielded a vent rate of about 20 Mg/yr. The packed column steam stripper processed about 42 L/min of water that contained primarily methylene chloride and chloroform. Total VO removal averaged 99.999 percent with an average concentration of less than 37 ppb in the bottoms. The condenser removed about 91 percent of the organic vapors and yielded a condenser vent rate of 11 Mg/yr. Emissions from the solids decanter and storage tank were estimated as 46 Mg/yr. The tray column stripper processed water containing 1.4 g/L of filterable solids compared to 0.01 g/L for the packed column. Costs for the small unit were confidential; the costs for the larger steam stripper were about $0.89/1,000 L treated.

The steam stripping/carbon adsorption unit was used to remove semivolatiles from water, which contained nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene. Steam stripping reduced the concentration from 634 ppm to 48 ppm, a reduction of 92 percent. Liquid-phase carbon adsorption decreased the concentration in the bottoms to below detection limits (0.8 ppm) and yielded an overall removal efficiency of greater than 99.6 percent. Maximum air emissions were estimated as 35 kg/yr. The total cost of treatment was estimated as $8.90/1,000 L treated.

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SECTION 1

INTRODUCTION

BACKGROUND

The Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) is developing regulations under the 1976 Resource Conservation and Recovery Act (RCRA) and its 1984 amendments to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDF). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile compounds and particulate matter.

Sources of volatile organic (VO)* emissions include storage tanks, treatment processes, surface lagoons, landfills, land treatment, and drum storage and handling facilities. Approximately 5,000 TSDF locations exist in the United States where one or more of these activities is in progress. Most of these sites are part of industrial facilities, and the rest are commercial facilities that accept wastes from offsite.

Research has concentrated on the characterization of uncontrolled emissions from these sources by using field measurements and by determining the reliability of emission models. Recent investigations have identified a number of options for controlling VO emissions from TSDF. These include restricting the VO concentrations of wastes going to sources where emission rates would be high, i.e., the "pretreatment" of waste to remove volatiles, and the use of in-situ (i.e., add-on) control techniques at the TSDF.

Pretreatment is in current use at several TSDF. In general, it is attractive because it can be used by either the waste generator or the TSDF operator to remove volatiles from the waste before they can be emitted into the air. Pretreatment may be a cost-effective control technique for TSDF emission sources with large surface areas, such as land treatment facilities and lagoons. For disposal surface impoundments (e.g., evaporation ponds) and aeration tanks and lagoons, pretreatment appears to be an important option because these TSDF processes rely on transfer of water or oxygen between the waste and the atmosphere as part of the disposal or treatment process, making process covers unattractive.

PURPOSE OF THE PROGRAM

The purpose of these investigations was to collect data for the support of regulations that consider waste pretreatment as an alternative for the control of volatile air emissions from TSDF. To the extent possible, these data were collected from processes that were treating hazardous wastes or that were

* For the purposes of this report, the term "volatile organic (VO)" refers to the combination of purgeable organics (eg, as detected in water using EPA Method 624) and extractable organics (eg, as detected in water using EPA Method 625). The terms "volatiles" and "semi-volatiles" are used at some points to refer to purgeable organics and extractable organics, respectively.

treating wastes with physical characteristics similar to hazardous wastes in order to permit a comparison of pretreatment to other emission controls.

Field data collected on several waste treatment techniques helped determine (1) how efficiently they remove volatiles from hazardous waste streams, (2) what the removal costs are, (3) how the byproducts from the pretreatment technologies are collected and disposed of, and (4) what limitations (in terms of waste types, volatile concentrations, etc.) are placed on the use of such treatment techniques.

PROCEDURES

The processes selected for evaluation included a pilot-scale thin-film evaporator used to treat refinery sludge, two steam strippers used to remove purgeable organic compounds from industrial wastewater, and one steam stripper used in combination with liquid-phase carbon adsorption to remove semivolatile organic compounds from wastewater. Preliminary site visits were conducted to observe and discuss the process operation and to collect information on process limitations, costs, operating conditions, and potential sampling points. During the preliminary visits, samples were taken for screening to identify the organic compounds and concentrations in the waste streams.

Detailed sampling and analysis plans, which also included the quality assurance plan, were written for each site. These plans provided details on the proposed sampling and analytical approaches, sampling points and number of samples, and the quality assurance/quality control (QA/QC) procedures and goals. Liquid samples taken for VO analyses were collected in vials with no headspace and included samples of the waste before and after treatment. Samples of process residuals, such as sludge, recovered organics, and air emissions, were also taken. Vapor samples were collected in evacuated and electropolished stainless steel containers. These samples were analyzed for organic compounds by gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) procedures. Additional details on the sampling procedures are given in Appendix A, and details of the analytical procedures are given in Appendix D. QA results are discussed in Appendix E.

The data were analyzed to determine the process removal efficiency for the specific organic compounds found in the waste. Removal efficiencies were calculated for each constituent and for total VO. Measurements of vent flow rates and vapor concentrations were used to calculate or estimate air emissions from the process. Process residuals were characterized in terms of quantity and VO content. In addition, cost data were collected and evaluated to provide an assessment of the total cost of the process and the cost-effectiveness for VO removal.

SCOPE OF THE REPORT

This report documents the use of three different processes at four sites to remove VO from waste streams. The first process was a thin-film evaporator that was used in a pilot-scale study to evaluate the treatment of refinery sludges. The results of this study are given in Section 3. Steam

strippers used in the chemical industry to remove purgeable organics were evaluated at two sites. These results are discussed in Section 4. The third process was a continuous steam stripper that also used liquid-phase carbon adsorption to remove semivolatile organic compounds from aqueous wastes. The results of this field test are given in Section 5.

Conclusions for all four sites are given in Section 2. A summary of process limitations and comparisons is provided in Section 6. Additional details are provided in the appendixes for sampling procedures, analytical procedures, process data, and QA/QC data.

SECTION 2

CONCLUSIONS

GENERAL CONCLUSIONS

1. Each of the processes investigated successfully removed VO from the wastes. The thin-film evaporator (TFE) removed over 99 percent of the VO from petroleum refinery sludge, the two chemical industry steam strippers removed 99.8 to 99.999 percent of the VO (purgeable organic compounds) from the wastewater, and the steam stripper/carbon adsorber removed 99.6 percent of the VO (primarily semivolatiles) from aqueous wastes. The results are summarized in Tables 2-1, 2-2, and 2-3.

2. Table 2-1 shows that steam strippers can reduce purgeable volatile organics from 6,000 ppm to ppm levels (<9.8 ppm) at Plant H or to ppb levels (<37 ppb) at Plant I. Semivolatiles may be reduced by steam stripping from over 600 ppm to about 48 ppm as shown in Table 2-2. Carbon adsorption of these semivolatiles reduced concentrations to below detection limits (<0.8 ppm). The TFE generally reduced volatile compounds by over 99 percent. Semivolatiles such as naphthalene and methylnaphthalene were removed efficiently (85-97 percent) at the higher temperature runs (Table 2-3).

3. The applicability of each of these processes depends in part on the solids content of the wastes. The TFE can handle sludges that contain high-boiling oils (17 to 25 percent oil) and solids (2 to 3 percent solids). The steam stripper tests showed that solids may need to be removed prior to steam stripping to 0.01 g/L (as done at Plant I) or the operator may experience fouling and frequent cleaning (as seen at Plant H with 1.4 g/L). Solids removal prior to steam stripping generates a sludge containing VO that may be a troublesome disposal problem.

4. The various processes that generate air emissions are preliminary treatment tanks (e.g., solids decanters), feed and storage tanks, condensate collection and storage tanks, and process vents (e.g., condenser vents). Condenser efficiencies for volatile organics ranged from 91 percent (cooling tower water at 21 °C) to 99 percent for a condenser cooled with refrigerated glycol (2 °C).

THIN-FILM EVAPORATOR (TFE) CONCLUSIONS

1. TFEs are able to process nonhomogenous feed streams such as oily refinery sludges. The major process limitations are that the feed and bottoms product must be pumpable and the feed should not foam excessively during processing.

TABLE 2-1. SUMMARY OF STEAM STRIPPER PERFORMANCE FOR PURGEABLE VOLATILE ORGANICS

Compound	In (ppm)	Out (ppm)	Percent reduction
PLANT H			
1,2-Dichloroethane	5,630	0.097	99.998
Chloroform	271	9.6	96.5
1,1-Dichloroethane	11	<0.01	>99.9
1,2-Dichloroethene	8.9	<0.01	>99.9
Vinyl chloride	8.4	<0.01	>99.9
1,1,2-Trichloroethane	7.5	<0.01	>99.9
Other volatiles	14	<0.01	>99.9
Total	5,950	<9.8	>99.8
PLANT I			
Methylene chloride	4,490	0.011	99.999
Chloroform	1,270	0.006	99.999
Carbon tetrachloride	55	<0.005	>99.99
Chloromethane	33	<0.005	>99.98
Other volatiles	11	<0.005	>99.95
Total	5,860	<0.037	>99.999

TABLE 2-2. SUMMARY OF STEAM STRIPPER AND CARBON ADSORBER PERFORMANCE FOR SEMIVOLATILES (PLANT G)

	Nitrobenzene	2-Nitrotoluene	4-nitrotoluene	Total
Concentrations (ppm)				
To stripper	505	78	51	634
From stripper	41	2.4	4.4	48
From adsorber	<0.8	<0.8	<0.8	<2.4
Percent reduction				
Stripper	92	97	91	92
Adsorber	>98	>67	>82	>95
Overall	>99.8	>98.9	>98.4	>99.6

TABLE 2-3. SUMMARY OF THIN-FILM EVAPORATOR RESULTS FOR TWO TEMPERATURES

Compound	In	Out[a]	Percent reduction	Out[b]	Percent reduction
Toluene	2,800	5.8-6.1	99.8	2.7-4.6	99.8-99.9
2-Methylnaphthalene	790	320-660	16-59	99-120	85-87
Naphthalene	765	160-520	32-79	24-46	94-97
m-Xylene	280	1.3-3.8	99-99.5	0.7-0.9	99.7-99.8
o,p-Xylene	280	1.4-4.4	98-99.5	0.7-0.9	99.7-99.8
Benzene	230	<0.01-1.0	99.6->99.9	<0.01-0.6	99.7->99.9
Ethylbenzene	180	0.7-2.1	99-99.6	0.4-0.6	99.7-99.8
Styrene	160	0.8-2.5	98-99.5	1.2-1.6	99-99.3

[a]From Runs 5 and 7 at 150 °C.

[b]From Runs 8 and 10 at 320 °C.

2. The TFE was found to have very high removal efficiencies of VO compounds from the waste sludges that were tested. In each of the three methods used to assess the reduction of volatiles, the removal efficiencies for VO compounds were greater than 99 percent.

3. The removal efficiency for VO was greatest when the TFE was operated at the highest temperature (320 °C). VO removal at this temperature generally exceeded 99 percent, with no clear trends relative to changes in feed rate.

4. The percent of semivolatiles removed from the feed ranged from 10 to 75 depending on the TFE operating conditions.

5. There were difficulties when the system was operated at high temperature (320 °C) under vacuum, as some carryover of feed into the condensate was observed. The condensate from the vacuum runs was a milky-white emulsion that would require additional treatment to separate the oils.

6. The gas flow rates and total VO emissions from the TFE condenser were highly dependent on the waste being processed. The first waste, an emulsion tank sludge, showed only minimal (less than 250 mL/min) flows from the condenser, and the second waste, oily tank bottoms, showed much higher (0.75 to 10 L/min) vent gas flow rates. All of the condenser vent gas concentrations were greater than 10,000 ppm (reported as hexane). The high VO concentrations in the vent gas were due to the vapor pressure of light hydrocarbons at the cooling water temperatures. A glycol-cooled condenser, a two-stage condenser (first stage cooling water, second stage chilled glycol), an incinerator, or some other appropriate control device could be used to reduce these emissions. The condenser and vent gas control system should be designed specifically for the waste to be treated because different wastes may contain different quantities of noncondensible or difficult-to-condense compounds.

7. The approximate capital and operating costs of TFEs when used to process petroleum waste sludges using various operational modes range from comparable to less than the cost of conventional land treatment. The cost of TFE sludge treatment was either $27.60, $40.60, $97.40 or $128/Mg depending on the mode of operation as compared to a cost of $110/Mg for land treatment. The process does not eliminate land treatment and the cost analysis assumes that the sludge from the TFE is disposed of by land treatment.

PLANT I STREAM STRIPPING CONCLUSIONS

1. The steam stripper reduced the total VO concentration by over 5 orders of magnitude from a feed concentration of roughly 6,000 ppm (0.6 percent) to less than 0.037 ppm. The removal of total VO was approximately 99.999 percent.

2. The primary condenser removed about 91 percent of the total VO in the vapors. Efficiencies for individual constituents ranged from 89 percent for chloromethane to 94 percent for chloroform.

3. The secondary vent condenser (with cooling tower water) did not appear to provide measurable control or condensation of VO. Theoretical calculations indicate that using refrigerated glycol cooling on the secondary condenser may improve its control efficiency for total VO to 68 percent.

4. The major air emission sources for the process are the solids decanters, storage tank, and noncondensibles from the steam stripper. Emissions were estimated as 2.7 grams (g) per L of water treated. For an average treatment rate of 41.6 liters per minute (L/min) or 11 gallons per minute (gal/min) for 75 percent of the year, annual emissions are estimated as 44 megagrams per year (Mg/yr) or 1.4 grams per second (g/s). These annual emission estimates assume a constant feed concentration of 6,000 ppm.

5. The vapor flow rate from the primary condenser when it was vented directly to the atmosphere was measured as 57 L/min. The emissions were measured as 2.4 g/L of water treated or 39 Mg/yr (1.2 g/s) for operation for 75 percent of the year. When the primary condenser was vented to the secondary condenser, the flow rate from the secondary condenser was measured at 11 to 13 L/min with an emission rate of 0.5 g/L of water treated or 8.2 Mg/yr (0.26 g/s) for operation for 75 percent of the year. The difference in measured flow rates (57 versus 11 to 13 L/min) suggests that some flow was not sampled because of leaks in the overhead system, overflow pipes, or tank vents. The estimates of annual emissions are based on the conditions during the test with an average feed concentration of 6,000 ppm.

6. Cost data supplied by the company were classified as Confidential Business Information (CBI) and are not included in this report.

PLANT H STEAM STRIPPING CONCLUSIONS

1. The steam stripper reduced the total VO concentration by approximately 3 orders of magnitude from a feed concentration of roughly 6,000 ppm (0.6 percent) to an average of 9.7 ppm. Removal of the major constituent (1,2-dichloroethane) consistently exceeded 99.99 percent.

2. The cost-effectiveness of the steam stripping operation was approximately $220/Mg of VO removed.

3. The overhead condenser removed 99+ percent of the total VO in the overhead vapors. The condenser efficiency was much lower for specific individual compounds present at low parts per million levels in the stripper influent.

4. The flow rate from the condenser vent ranged from 1.9 to 4.2 L/s (4.0 to 8.8 ft^3/min). The condenser vent on this steam stripper was routed to an incinerator. A similar system vented to the atmosphere could emit 12 to 51 Mg/yr of VO.

5. Steam usage for this steam stripper appeared to be optimized because it was lower than values observed for other steam strippers and was also lower than values given in design manuals.

6. The removal of all constituents was consistently high except for chloroform. The variations in chloroform removal appear to be related to fouling from the accumulation of solids. Suspended solids concentrations in the stripper influent were on the order of 0.1 percent.

7. The major operational problem experienced with this steam stripper is the fouling of the heat exchanger and column trays. Solids removal prior to the steam stripper may provide a more consistent operation. The results indicate that a steam stripper can be operated for wastewater containing 0.1 percent solids if the operator is willing to backflush and clean the system periodically. However, if the solids are removed prior to steam stripping, the resulting sludge may be a troublesome disposal problem and an additional source of VO. Consequently, the company has chosen to incur the additional cost of cleaning the existing system periodically instead of installing equipment for the removal, treatment, and disposal of solids.

PLANT G STEAM STRIPPING/CARBON ADSORPTION CONCLUSIONS

1. Semivolatile organic compounds can be removed from wastewater using steam stripping and carbon adsorption. Removal efficiencies of 92 percent were observed for the steam stripper, and the carbon adsorber removed more than 95 percent of the organics fed to it. The removal efficiency of the combined steam stripper-carbon adsorber was greater than 99.6 percent.

2. Air emissions from the condenser vent were very low, and the gas flow from the vent could not be measured reliably. Concentrations of VO in the vent stream varied widely, with total VO (as ppm hexane) between 10 and 2,000 ppm. The maximum air emissions were estimated to be 4.0 g/h.

3. Carbon was added to the adsorbers in a pulse feed mode an average of 1.5 times per day, with a carbon addition of 908 to 1,360 kg/charge. The carbon was regenerated offsite and was the major cost of the process. The organic concentrations of the wastewater fed to the adsorber were relatively low (47.8 ppm), and utilization of the carbon was correspondingly low (0.021 kg organics removed/kg carbon used). The total annualized cost of the steam stripper-carbon adsorption system was $14.30/kg organics removed.

4. The high normalized operating costs of the system resulted primarily from the low feed concentrations (634 ppm organics) and the high removal efficiency (>99.6 percent) of the steam stripper carbon adsorber. On a water-processed basis, the total annualized cost was $0.0089/kg water treated (or 0.89 ¢/L).

5. Approximately 78 percent of the steam used in the steam stripper was condensed into the water being stripped, and 22 percent was condensed with the stripped organics. This condensation into the stripped liquid produces a varying gas/liquid (G/L) ratio within the column: 55 m^3/m^3 at the base and 24 m^3/m^3 at the top. The heat exchanger, used to heat the feed with the bottoms from the stripper column, reduced the steam requirements for the column.

6. Principal variables influencing the effectiveness of the process were the feed rate and steam rate of the process. Downtime of the process was reported as less than 1 percent of operating time, with heat exchanger fouling as the only maintenance problem.

SECTION 3

RESULTS OF THE THIN-FILM EVAPORATOR TESTS

DESCRIPTION OF PILOT FACILITY

The tests were conducted at the pilot facility of a manufacturer of TFEs (Luwa Corporation, Charlotte, NC). This facility contains a variety of evaporators produced by the company and is used to test potential applications of their equipment for clients. Consequently, the equipment used for the tests was configured specifically for our applications. This pilot facility was used to evaluate the effectiveness of a TFE for the removal of VO from petroleum waste sludges. Samples of tank bottoms sludge were obtained from an oil company refinery, tested in the equipment, and then returned to the refinery for normal disposal.

Figure 3-1 shows the equipment used in the pilot-scale tests. The 380-L (100-gal) feed tank was agitated with both an axial mixer and continuous recirculation of the feed liquid through a centrifugal pump. A Moyno positive displacement pump was used to pump the feed sludge through the preheater and into the top of the TFE. The sludge was continuously spread over the heated surface of the TFE as it progressed down through the TFE to a collection pot at the base. Materials evaporating in the TFE passed through an empty entrainment separator (demister) and were condensed in a condenser that was cooled with cooling tower water. Condensate flowed from the condenser and was collected directly into liquid sample jars or a flask used for measuring condensate flows. Any uncondensed vapors flowed from the condenser through a wet testmeter for flow measurement.

The TFE was heated by hot oil, although steam could be used for lower temperatures. Entrainment separators are used frequently with TFEs to remove entrained liquids from the vapors flowing to the condenser. The entrainment separator was empty (but heated) during the testing, and very little material condensed in the entrainment separator. The feed lines from the preheater to the TFE were heated with low-pressure steam, as were the vapor lines from the TFE through the entrainment separator and to the condenser. Table 3-1 is a complete list of the process equipment used in the tests.

In actual operation, TFEs require relatively little maintenance and operator supervision. Feed material is usually charged to a feed tank, the equipment is preheated, and processing is started. Condensate and bottoms are collected separately and emptied periodically by an operator. During the pilot tests, three Luwa personnel operated the equipment, measured flow rates, and collected samples. This was necessary because of the relatively rapid changes in operating conditions and the extensive sampling of the process.

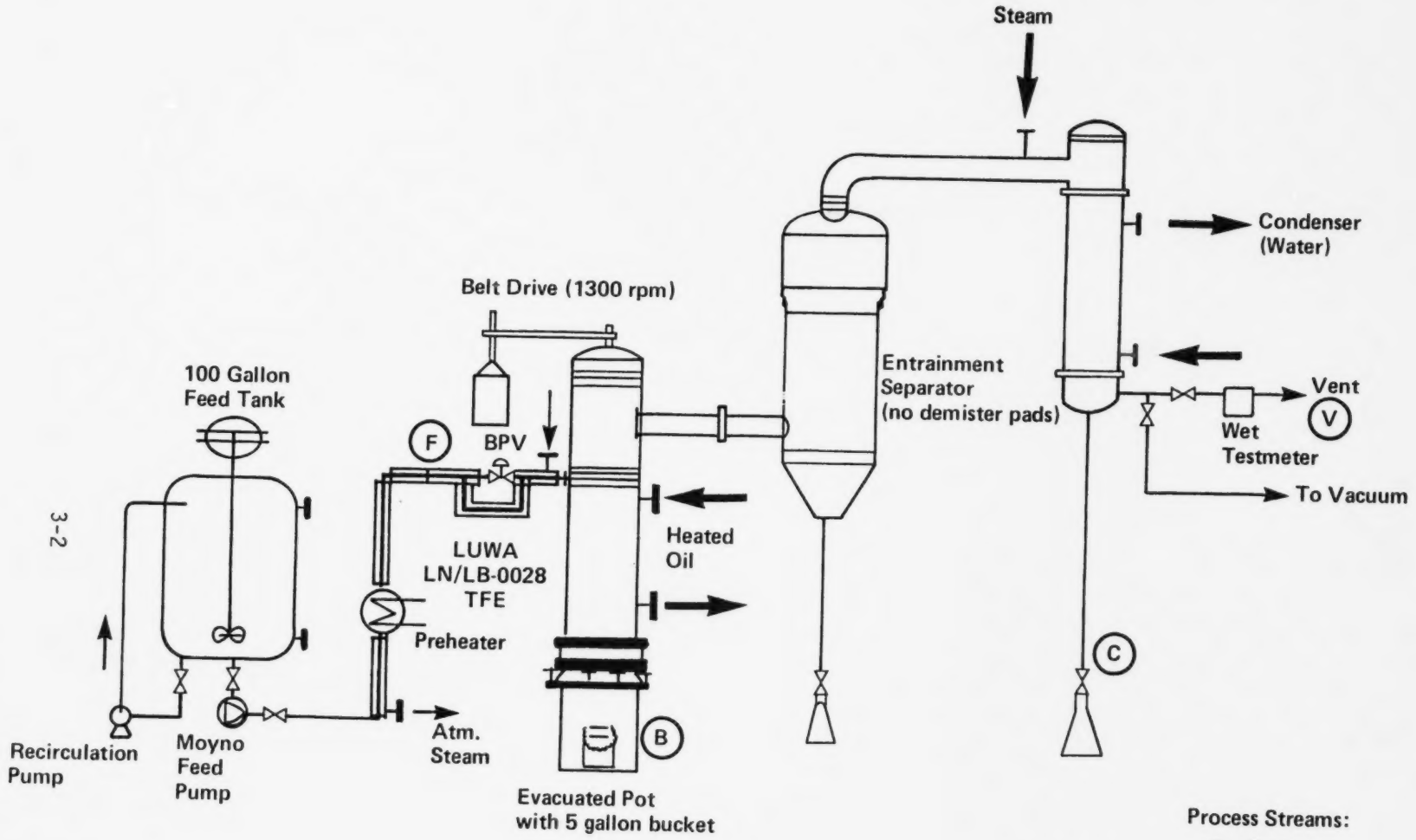

Figure 3-1. Configuration of test equipment.

TABLE 3-1. PROCESS EQUIPMENT SPECIFICATIONS

Test Unit:	Luwa thin-film evaporator type LN-0028, 3.02 ft^2 thermal surface area heated with oil
Lubrication:	Upper seal - water Lower bearing - roller
Rotor drive:	1.5 hp, 440 V, three phase

Auxiliary equipment specifications

Feed from:	100-gal jacketed feed tank with agitator and recyle pump
Feed pump:	MOYNO positive-displacement pump with variable speed drive
Feed preheater:	15 ft^2 shell-and-tube type heat exchanger heated with controlled steam
Condenser:	15 ft^2 shell-and-tube type heat exchanger cooled with tower water
Bottoms receiver:	Evacuated pot containing 5-gal bucket
Distillate receiver:	4,000 mL flask
Material of constant:	Stainless steel, type 304 and 316

The major maintenance on field units is periodic replacement of the feed pump and bottoms pump. The frequency of required replacement is highly dependent on the materials processed, with abrasive feedstocks wearing out the pumps more rapidly than nonabrasive feeds. In this test progressive failure of the Moyno feed pump was noted and determined to be due to polymers in its rotor and cavity absorbing hydrocarbons in the feed sludge, reducing the pump's effectiveness.

TESTS PERFORMED WITH THIN-FILM EVAPORATORS

A total of 22 tests were performed with the TFE, using two different wastes, three temperatures, three flow rates, and under both atmospheric and vacuum operation. The feed rates and temperatures were chosen to operate the TFE over its normal range of operation and to demonstrate the removal of VO from the feed sludges. The testing occurred over 1 week at the Luwa Corporation pilot-test facility in Charlotte, NC (September 8 to 11, 1986).

Both waste sludges tested were provided by the same oil company and were shipped to the Luwa test facility in 55-gal drums. Tests 1 through 18 used five 55-gal drums of the first waste, an emulsion tank sludge, while tests 19 through 22 were performed on the second waste sludge, oily tank bottoms. The process testing, sampling, and analysis concentrated on the tests using the first waste while the second waste was used to gather additional process data and demonstrate process operation on a second waste sludge. During the first day of testing (September 8, 1986), the first two barrels of the first waste were charged to the feed tank. Although the sludge was well mixed prior to charging and agitated in the feed tank, it separated into two layers. The water-rich layer at the base of the feed tank was pumped into the TFE, producing very little bottoms and more water than expected in the condensate. Once this problem was discovered, an additional recycle pump was installed on the feed tank to better mix the sludge and prevent it from splitting into two phases. The remaining sludge in the tank was used for the first four shakedown runs on September 9, 1986, which were not used as part of the test plan. This allowed practice samples to be taken and potential problems to be solved prior to adding a new drum of waste to the feed tank for use in the actual test runs.

The basic test plan (and run numbers for the tests) is shown in Table 3-2. This test plan studied the two major variables affecting TFE performance--the temperature of the heating jacket and the feed rate. The indicated flows and temperatures were the nominal process parameters during the test, and the actual measured parameters varied somewhat from these values. Shakedown runs 1, 2, 3, and 4 were performed with the remainder of the first two barrels of waste that experienced a phase split on September 8, 1986. Test runs 5, 6, and 7 were a series of tests at a constant heating jacket temperature (150 °C) at three different feed rates. Runs 8, 9, and 10 were conducted at similar flow rates to runs 5, 6, and 7 but were at a much higher heating jacket temperature (320 °C). Runs 12, 13, 14, 15, and 16 were conducted at an intermediate temperature (230 °C) and were limited to the two lower flow rates because of the progressive failure of the Moyno feed pump. This pump was equipped with a polymeric-based rotor and stator, which absorbed minor amounts

TABLE 3-2. TEST MATRIX FOR THIN-FILM EVAPORATOR TESTS

Tests with feed No. 1, emulsion tank bottoms:

Temperature (°C) =	150	230	310
Flow rate (lb/h)			
70	RUN 5	RUN 14	RUN 8
100	RUN 6	RUN 15 RUN 16	RUN 9
150	RUN 7		RUN 10

Vacuum runs:

Run 11: 320 °C, 23 lb/h
Run 17: 150 °C, 57 lb/h
Run 18: 100 °C, 57 lb/h

Tests with feed No. 2, oily tank bottoms:

Temperature (°C) =	150	310
Flow rate (lb/h)		
45	RUN 21	RUN 19
80	RUN 22	RUN 20

of feed hydrocarbons, degrading pump performance. Runs 12 and 13 were shakedown tests at the intermediate temperature.

Three vacuum runs were performed with the first waste sludge during runs 11, 17, and 18. These runs were to examine the effect of vacuum operation on the removal of VO from the feed waste. One run (#11) was at high temperature and a very low feed rate. This run was to demonstrate the large volume reduction of bottoms that result when the system is operated at high temperatures and under vacuum. The two low-temperature vacuum runs (17 and 18) were to discover whether the process could achieve substantial removal of volatiles and water at lower temperatures (vacuum reduces the boiling point of water, decreasing the operating temperature of the TFE). The final four runs (19, 20, 21, and 22) were performed with the second waste. These tests were principally to demonstrate the operation of the TFE with a second waste sample and were not extensively sampled and analyzed during the project.

Four of the tests (5, 7, 8, and 10) were selected for extensive sampling and analysis of process streams. These four runs allowed the process to be examined with both high and low feed rates and at both high and low heating temperatures. They represent the range of reasonable operating conditions for the TFE processing waste sludges for the removal of volatiles, water, and oils from the sludge.

The complete operating process conditions, flow rates, and aqueous/organic splits of the condensate are shown in Table 3-3. Table 3-4 summarizes the organic/aqueous splits that occurred in the collected samples. Relevant features of the process results are described below:

1. The three runs at 150 °C (5, 6, and 7) show only a slight decrease in condensate flow (16.4 to 14.6 lb/h) as the feed rate was increased from 72 to 154 lb/h. The temperature of the bottoms from the TFE remained constant near 100 °C, indicating that water was still evaporating from the bottoms as it left the evaporator. This shows that at low temperature the process was heat transfer limited, with an almost constant amount of material being evaporated from the feed regardless of feed rate. Figure 3-2 shows the condensate flow rate as a function of the feed rate. The condensate flow rate decreased slightly as the feed rate was increased because of the additional heating of the feed sludge from about 70 to 100 °C. The organic condensate flow rate increased proportionally with the increases in feed rate, showing that the organics more volatile than water were being evaporated from the feed and recovered as organic condensate. The aqueous flow rate shows exactly the opposite relationship--as the feed rate increased, the aqueous condensate flow rate decreased. Figure 3-3 shows the bottoms flow rate for the same set of data. The bottoms flow rate from the process increased proportional with the feed rate, with the bottoms containing unevaporated water, oils, and solids.

2. The three runs at 320 °C (8, 9, and 10) showed a substantially different variance of condensate flow rate with feed rate. Figure 3-4 shows that the condensate flow rates for these runs were much higher than for the lower temperature runs, and the bottoms temperatures were 216,

TABLE 3-3. RUN PROCESS CONDITIONS AND FLOW RATES

LUWA Run #	Operating pressure, mm Hg	TFE Heating		Feed stream		Bottoms		Condensate									Bottoms produced, % of feed
		In, °C	Out, °C	Temp, °C	Flow rate, lb/h	Temp, °C	Flow rate, lb/h	Vapor temp, °C	Condensate temp, °C	Flow rate, lb/h	Organic fraction			Aqueous fraction			Oil recovered, % of feed	Water recovered, % of feed	
											% of condensate	Flow rate, lb/h	Density, g/mL	% of condensate	Flow rate, lb/h	Density, g/mL			
5	ATM	150	150	82	71.6	98	55.2	85	26	16.4	0.106	1.74	0.864	0.894	14.66	0.997	2.4	20.5	77.1
6	ATM	150	150	78	107.8	102	93	86	26	14.8	0.143	2.12	0.812	0.857	12.68	0.994	2.0	11.8	86.3
7	ATM	150	150	74	153.7	100	139	88	26	14.6	0.103	2.67	0.796	0.817	11.93	0.995	1.7	7.8	90.4
8	ATM	320	322	73	68.5	104	8.5	50	24	60	0.113	6.78	0.840	0.887	53.22	0.991	9.9	77.7	12.4
9	ATM	336	326	60	113.7	216	11.7	71	28	102	0.127	12.91	0.858	0.873	89.09	1.000	11.4	78.4	10.3
10	ATM	318	306	60	143.4	200	10.6	72	28	124.8	0.103	12.87	0.834	0.897	111.93	0.993	9.6	78.1	13.0
11	45	339	334	42	23.2	142	1	52	29	22.2	0.593	13.17	0.960	0.407	9.03	0.993	56.7	38.9	4.3
13	ATM	234	228	38	82	104	22	70	30	60	0.081	4.85	0.854	0.919	55.15	0.987	5.9	67.3	26.8
14	ATM	236	228	72	68.2	124	10.2	72	38	58	0.083	4.79	0.836	0.917	53.21	0.990	7.8	78.8	15.6
15	ATM	234	228	68	94	100	28.4	72	30	65.5	0.084	5.50	0.835	0.916	60.00	0.989	5.8	63.8	30.2
16	ATM	234	228	68	111.5	100	46	73	36	65.5	0.077	5.02	0.831	0.923	60.48	0.991	4.5	54.2	41.3
17	45	150	146	68	57.2	55	34.8	65	32	22.4	0.077	1.72	0.831	0.923	20.68	0.991	3.8	36.2	60.8
18	45	102	100	42	57.8	52	48.2	72	36	17.6	0.044	0.77	0.810	0.956	16.83	0.994	1.3	29.1	69.6
19	ATM	341	337	84	53.6	196	8	55	30	46.6	0.424	19.32	0.914	0.576	26.28	1.000	38.8	49.6	14.9
20	ATM	346	334	83	80	215	12.8	62	30	67.2	0.362	24.30	0.820	0.638	42.90	0.998	30.4	53.6	16.8
21	ATM	151	149	80	41.3	100	26.4	92	34	14.9	0.303	4.52	0.788	0.697	10.38	0.997	10.9	25.1	63.9
22	ATM	151	149	82	77.6	100	54.2	76	34	23.3	0.277	6.45	0.778	0.723	16.85	0.993	8.3	21.7	69.9

TABLE 3-4. CONDENSATE ORGANIC/AQUEOUS SPLITS

LUWA run No.	Condensate samples	Aqueous			Organic			Organic/aqueous split weight % organic
		Volume, mL	Weight, g	Density, g/mL	Volume, mL	Weight, g	Density, g/mL	
5	LUWA-64,46	1,650	1,645.0	0.997	294	195.3	0.664	10.6
6	LUWA-49	810	805.1	0.994	166	134.8	0.812	14.3
7	LUWA-52,53	1,524	1,516.8	0.995	427	340.0	0.796	18.3
8	LUWA-71,72	1,665	1,649.2	0.991	250	210.0	0.840	11.3
9	LUWA-86	805	805.0	1.000	136	116.7	0.858	12.7
10	LUWA-89,90	1,718	1,705.7	0.993	235	196.1	0.834	10.3
11	LUWA-101	365	362.3	0.993	550	528.0	0.960	59.3
13	LUWA-112	885	873.6	0.987	90	76.9	0.854	8.1
14	LUWA-115	890	881.5	0.990	95	79.4	0.836	8.3
15	LUWA-118	885	875.4	0.989	96	80.2	0.835	8.4
16	LUWA-121	890	881.6	0.991	88	73.1	0.831	7.7
17	LUWA-124	890	881.6	0.991	88	73.1	0.831	7.7
18	LUWA-127	1,000	994.1	0.994	56	45.7	0.816	4.4
19	LUWA-133	510	509.8	1.000	410	374.8	0.914	42.4
20	LUWA-136	580	579.1	0.998	400	328.1	0.820	36.2
21	LUWA-139	635	632.8	0.997	350	275.7	0.788	30.3
22	LUWA-142	655	650.2	0.993	320	248.8	0.778	27.7

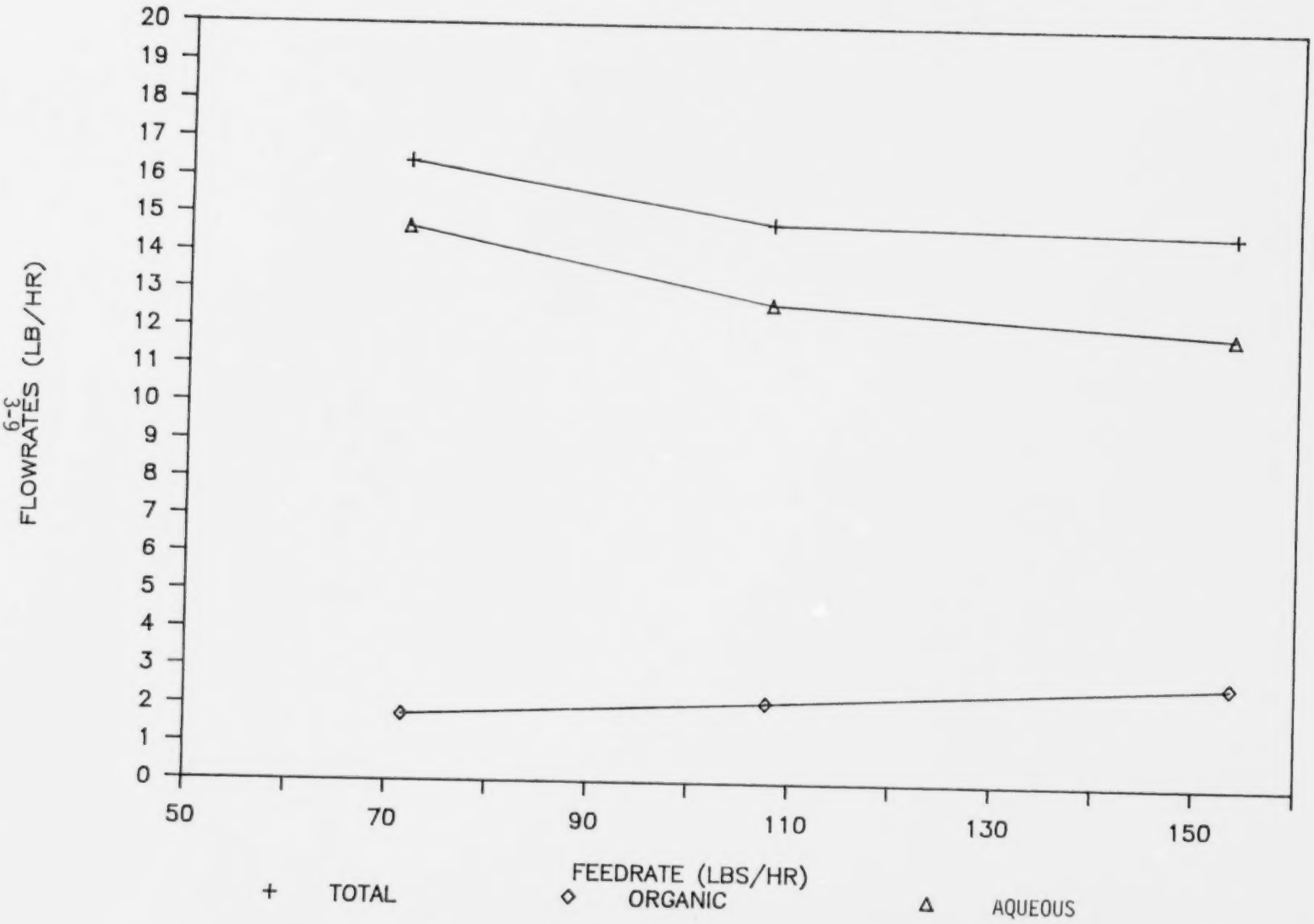

Figure 3-2. Condensate flow rates as a function of feed rate at 150 °C.

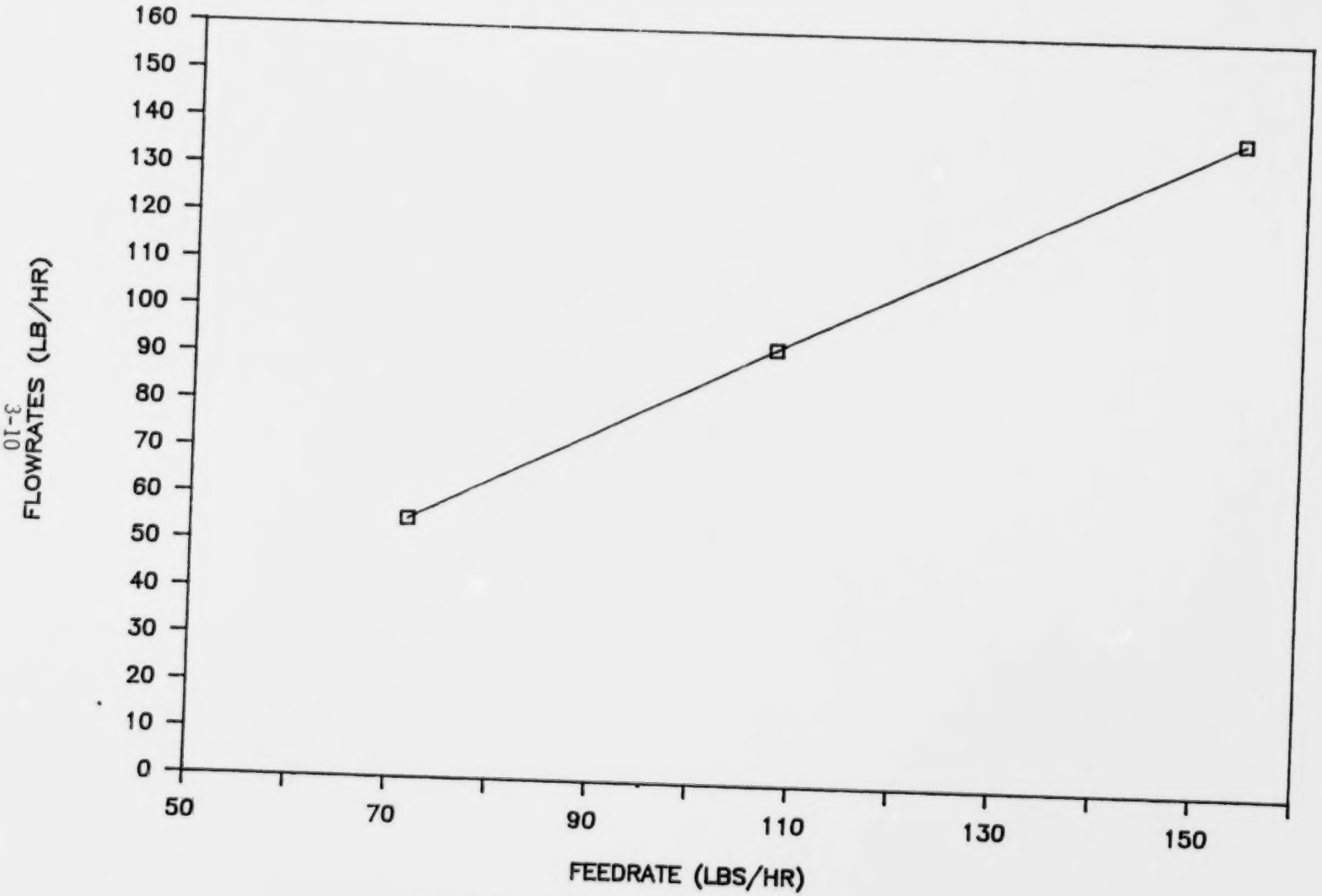

Figure 3-3. Bottoms flow rate as a function of feed rate at 150 °C.

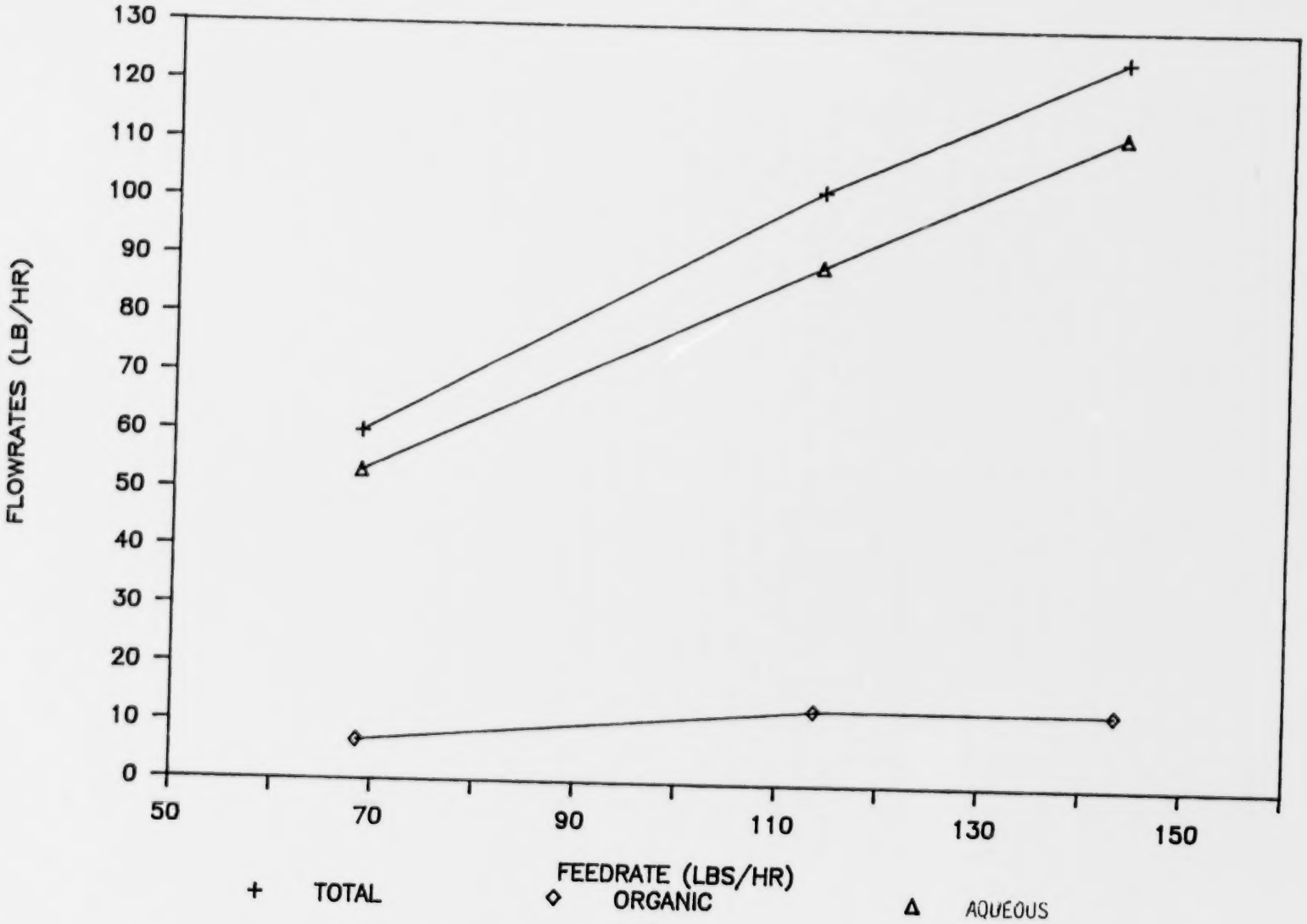

Figure 3-4. Condensate flow rates as a function of feed rate at 320 °C.

200, and 142 °C, with bottoms temperatures decreasing as flow rate increased. These temperatures show that nearly all the water contained in the feed was evaporated and that much of the heavier oils in the sludges were also evaporated. As the feed rate for this run increased, the total condensate flow rate and aqueous flow rates increased while the organic condensate flow rate showed an increase between 69 and 114 lb/h of feed and only a minor change between 114 and 143 lb/h feed. This is explained by examining the bottoms flow rate shown in Figure 3-5. The bottoms flow rate increased slightly between the two lower feed rates but jumped substantially between the two higher flow rates. There was only a 16° drop in bottoms temperature between the lowest and middle feed rates, while the bottoms temperature dropped 58° between the middle and highest flows. Consequently, the bottoms at the highest flow rate contain additional oils that vaporized at the higher temperature achieved in the lower flow rate runs.

3. The process results occurring at the intermediate temperature resemble the results at 150 °C. These tests were at 230 °C (runs 14, 15, and 16) and at flow rates between 68 and 112 lb/h. The highest flow rate obtained was 112 lb/h at the time of the tests, due to feed pump failure. Figure 3-6 shows the condensate flows for these runs. Although the condensate flow rate did increase with increases in feed rate, the increases were not proportional to flow rate increases. The bottoms temperatures for the four runs were 124, 104, 100, and 100 °C, with the bottoms temperature decreasing as feed rate increased. The bottoms temperature was above 100 °C only at the lowest flow rate (68 lb/h). For this run, almost all of the water would be evaporated from the feed, along with some of the oils boiling between 100 and 124 °C. As the flow rates increased, there was a higher rate of water feed into the TFE and the bottoms temperature dropped to 100 °C. The bottoms flows increased as feed rate increased (Figure 3-7), but more bottoms were produced as a percent of feed as the feed rate was increased, due to more water passing through the TFE and exiting with the bottoms.

4. The vacuum runs showed that some potential problems will likely occur if water/organic sludges are processed by TFE's under vacuum. The condensates for all of the vacuum runs formed a milky white emulsion of organics and water. This contrasted substantially with the clean splitting organic/aqueous layers that occurred during all of the atmospheric pressure runs. Such an emulsion would be relatively difficult to separate and would present processing problems. A simple solution to the formation of these emulsions would be to process the waste sludge with two passes through TFEs. The first TFE would remove the water and VO from the waste, producing easily handled condensate and oil fractions. The second TFE would operate at high temperature and under vacuum. The oils heavier than water would be removed as a single condensate, with a relatively low water content. The amount of bottoms for ultimate disposal would be only a small fraction of the original waste sludge, and would contain solids and the heaviest oils of the waste.

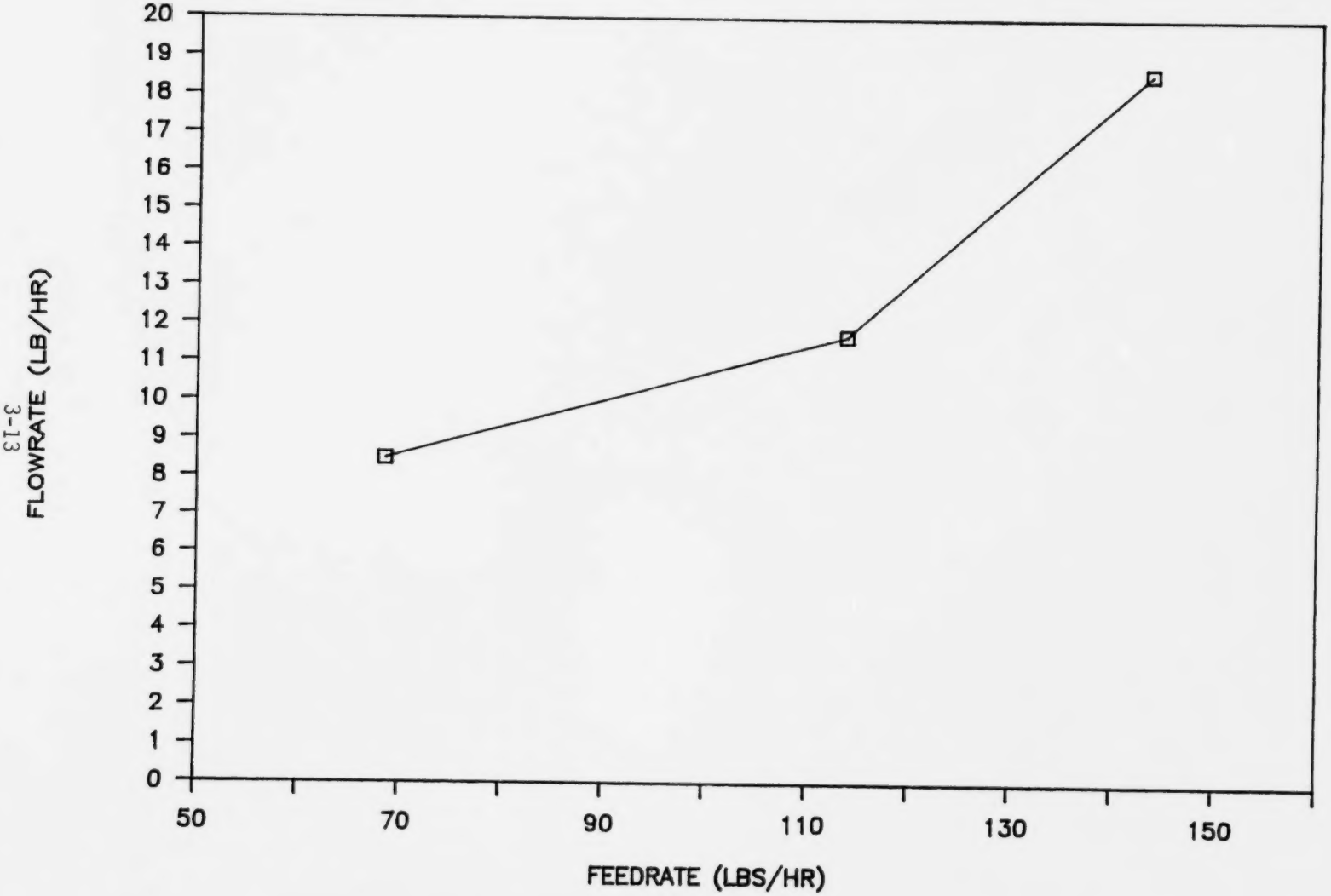

Figure 3-5. Bottoms flow rate as a function of feed rate at 320 °C.

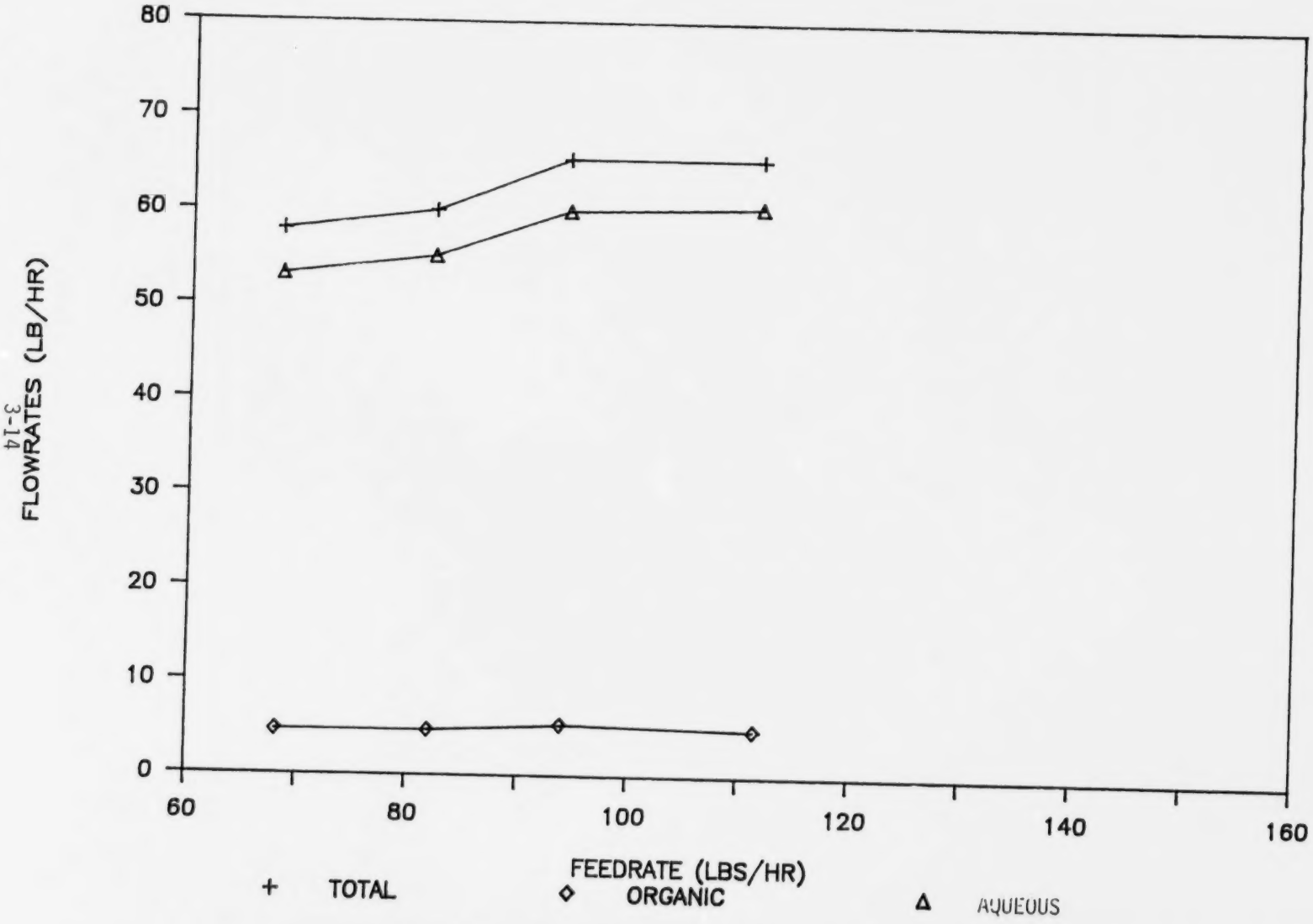

Figure 3-6. Condensate flow rates as a function of feed rate at 230 °C.

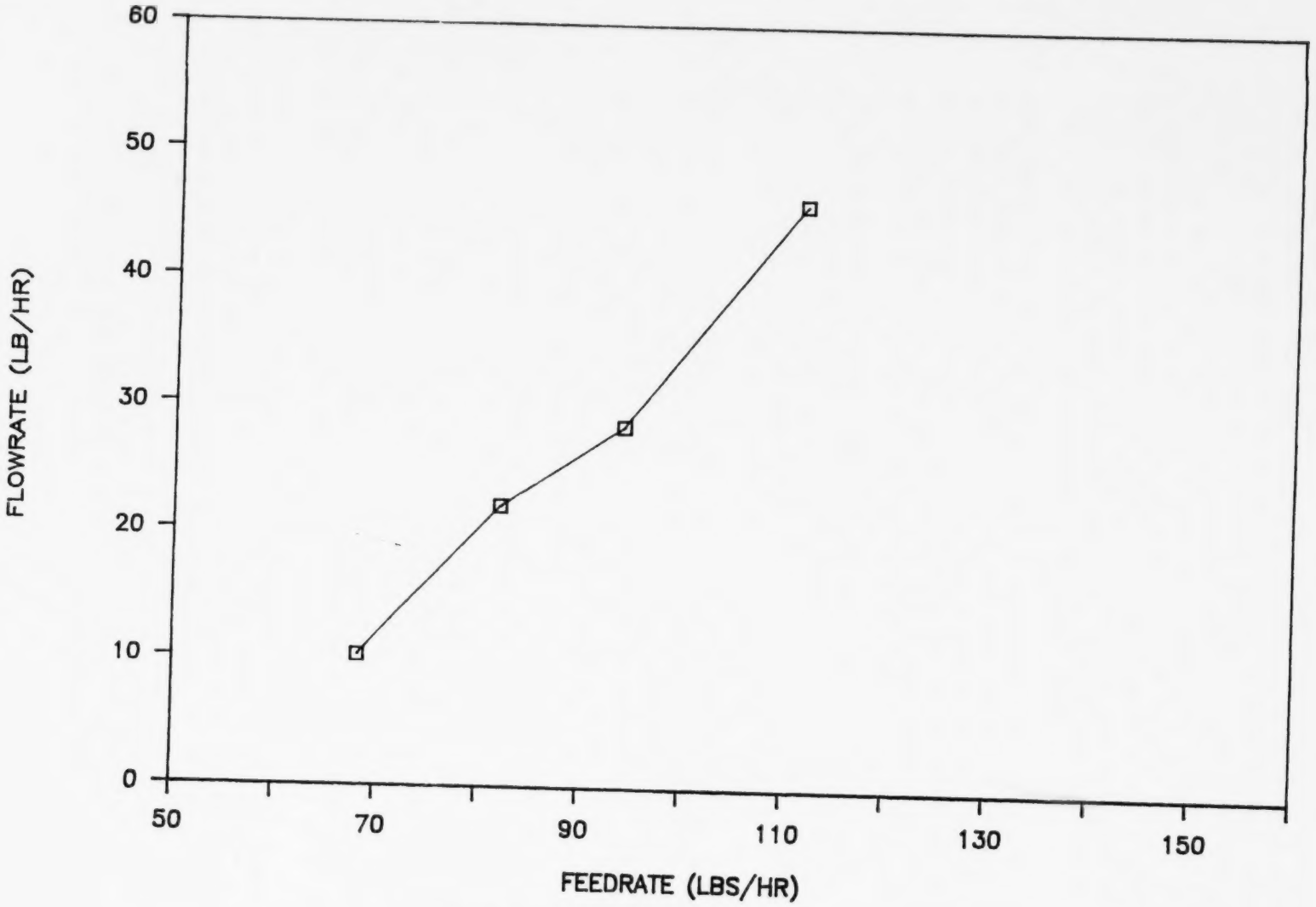

Figure 3-7. Bottoms flow rate as a function of feed rate at 230 °C.

The vacuum run at 320 °C (run 11) had substantial carryover of feed entering the TFE. The feed vaporized so rapidly at this temperature that raw feed was carried into the condenser and condensate. There was also substantial loss of volatiles through the condenser vent and through the vacuum system. The measured feed rate for this run (23.2 lb/h) was determined from the bottoms and condensate collected, so it is highly suspect. The density of the collected organic layer (0.96 g/mL) shows that it contained substantial water when it was separated from the aqueous layer. The listed percentage of oil recovered for this run refers to this oil/water emulsion, rather than a cleanly separated oil phase that occurred in the other runs.

This would be a very unrealistic set of conditions to operate the TFE on this type of waste sludge, although the very large reduction in the bottoms requiring disposal indicates that a two-stage TFE process would be appropriate where large reductions in the amount of waste for disposal are desired. The bottoms from the process were 4.3 percent of the measured feed rate and were a viscous high carbon oil.

The low-temperature vacuum runs (17 and 18) showed that water and volatiles could be recovered from the wastes at relatively low temperatures, but the emulsions formed in the condensate would present some difficulty. The bottoms temperature for these two runs were 55 and 52 °C, and the TFE was heated at 150 and 100 °C.

5. The second waste tested had a much higher oil content than the first. The two runs at 150 °C were heat transfer limited, with a bottoms temperature of 100 °C. The runs at 340 °C achieved much higher condensate rates and bottoms temperatures, removing substantially more oil and all the water from the waste. These results confirmed the process data gathered on the first feed and demonstrated the operation of the TFE on a second waste sample.

Three different methods were used to determine the effectiveness of the process for the removal of volatiles from the wastes. Two of these involved analytical methods applied at the test site during testing, and the third used samples collected and analyzed by a contract laboratory. These three methods all showed that the TFE process was very effective in the removal of volatiles from the wastes tested under essentially all of the conditions used for the tests. The measured percent removal was, in general, greater than 99 percent for all of the individual VO identified in the waste and also greater than 99 percent for the total VO in the wastes.

A portable GC was used to determine the concentration of VO in the headspace above half-filled sample bottles containing feed waste and bottoms product. Because both the feed samples and bottoms contain a high percentage of oil, the headspace concentrations of VO are proportional to the VO concentrations within the samples. By measuring the headspace concentrations (and the reduction in concentration after processing) the percentage of waste VO removal can be determined. This also has the advantage of determining the vapor concentrations above the raw feed and waste bottoms. The peaks were all detected with a flame-ionization detector (FID) and integrated with a portable

GC integrator. The analytical system was calibrated with both a C1 to C6 hydrocarbon standard (methane, ethane, propane, butane, pentane, and hexane) and a benzene standard. Toluene was injected to determine the retention time of that compound. Peaks were identified by both retention time on the GC column and an analysis of feed vapor headspace by GC/MS conducted later.

Table 3-5 shows the results of this analysis and the calculated percent reductions in headspace concentrations above the samples. In virtually all the samples, the reduction in headspace concentration was greater than 99 percent. The only exception to this occurred with the very light hydrocarbon propane. This is probably because these light hydrocarbons would tend to be much more in the vapor phase than the heavier hydrocarbons that are liquids at room temperature.

After the headspace of the samples was analyzed by GC analysis, a total hydrocarbon analyzer (Bacharach TLV) was used to measure the total hydrocarbons in the headspace above these samples. The results of this analysis are displayed in Table 3-6. Unfortunately, the Bacharach TLV has a maximum range of 10,000 ppm of hydrocarbons (measured as hexane). This limit was exceeded by the headspace of the feed samples, but the headspace of the bottoms samples was well within the range of the instrument. The calculated reductions in headspace concentration based on these data used 10,000 ppm hexane as the headspace concentration of volatiles in the feed waste. The actual concentration was greater than 10,000 ppm, thus the percent reduction figures are minimum reductions in concentration with the actual headspace concentration reductions expected to be higher than the percentages listed. Even with this limitation, the minimum reductions in volatiles were all 99+ percent (except runs 7 and 11, which were 98.8 and 98 percent, respectively). These results confirmed the headspace concentrations measured with the GC analysis in Table 3-5. The results of duplicate and triplicate samples gave very consistent analyses, as did the GC measurements of headspace concentration. It is interesting to note that the headspace concentrations for Runs 5, 6, and 7 (TFE temperature of 150 °C) increased with increasing flow rate (80, 98, and 120 ppm, respectively), and runs 8, 9, and 10 showed the reverse relationship to feed rate (78, 32, and 28 ppm, respectively). The high-temperature results may be due to some cracking of hydrocarbons at low flow rates at high temperatures. These trends were not observed with the GC measurements of headspace concentration.

The third measurement of volatile reduction involved the analysis of feed and bottoms samples for volatiles in the collected samples. Table 3-7 compiles the analytical results for VO in feed, bottoms, and condensate samples. These samples were from runs 5, 7, 8, and 10. One sample from each feed drum was analyzed along with the bottoms from each run. Only one sample of aqueous condensate was analyzed because the concentrations of organic compounds in this condensate phase were expected to be very small relative to the organic condensate samples. This was confirmed in the analysis of the sample. The analysis of feed sample Luwa-188 for volatiles appeared to be in error, perhaps because the sample split into two phases and the analyst used an aqueous sample from the feed. The surrogate recovery on this sample was very good, indicating that any analytical error occurred in the preparation of the sample rather than the analysis.

TABLE 3-5. REDUCTION IN HEADSPACE VOLATILE ORGANIC CONCENTRATIONS, FROM ONSITE GC ANALYSIS OF HEADSPACE

	Ave feed (n=8), µg/L	Run #5 bottoms ave, µg/L	Run #6 bottoms, µg/L	Run #7 bottoms ave, µg/L	Run #8 bottoms ave, µg/L	Run #9 bottoms, µg/L	Run #10 bottoms ave, µg/L	Run #11 bottoms ave, µg/L	Run #13 bottoms, µg/L	Run #14 bottoms, µg/L	Run #15 bottoms, µg/L	Run #16 bottoms, µg/L	Run #17 bottoms, µg/L	Run #18 bottoms, µg/L
Propane	121	1.6	3.8	2.3	2.6	0.9	1.4	0.9	16.9	14.0	20.7	8.3	11.2	5.9
Butane	1,065	4.4	12.4	7.1	6.3	2.3	2.9	BDL	9.9	4.2	12.2	11.2	8.9	4.0
2-Methylbutane	1,138	0.4	1.3	0.6	0.1	BDL	BDL	0.6	0.3	BDL	BDL	0.7	0.1	BDL
Pentane	1,029	0.9	2.5	1.0	1.6	BDL	BDL	0.5	0.8	BDL	0.5	1.4	0.5	BDL
2-Methylpentane	421	BDL	BDL	BDL	BDL	BDL	BDL	0.2	BDL	BDL	BDL	BDL	BDL	BDL
Benzene	1,516	2.3	2.5	1.7	5.0	BDL	BDL	1.2	BDL	BDL	0.8	BDL	BDL	BDL
Hexane	432	0.3	BDL	BDL	0.6	BDL	BDL	0.3	BDL	BDL	BDL	BDL	BDL	BDL
Toluene	1,143	10.8	4.9	5.3	5.1	BDL	BDL	9.4	0.7	BDL	BDL	BDL	BDL	BDL
% Reduction in headspace concentrations (where a component was not detected in the bottoms headspace, a value of 0.2 µg/L was used)														
Propane		98.72%	96.86%	98.10%	97.89%	99.26%	98.88%	99.26%	86.03%	88.43%	82.89%	93.14%	90.74%	95.12%
Butane		99.59%	98.84%	99.33%	99.41%	99.78%	99.73%	99.98%	99.07%	99.61%	98.85%	98.95%	99.16%	99.62%
2-Methylbutane		99.97%	99.89%	99.95%	99.99%	99.98%	99.98%	99.95%	99.97%	99.98%	99.98%	99.94%	99.99%	99.98%
Pentane		99.91%	99.76%	99.90%	99.84%	99.98%	99.98%	99.95%	99.92%	99.98%	99.95%	99.86%	99.95%	99.98%
2-Methylpentane		99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%
Benzene		99.85%	99.84%	99.89%	99.67%	99.99%	99.99%	99.92%	99.99%	99.99%	99.95%	99.99%	99.99%	99.99%
Hexane		99.93%	99.95%	99.95%	99.86%	99.95%	99.95%	99.93%	99.95%	99.95%	99.95%	99.95%	99.95%	99.95%
Toluene		99.06%	99.57%	99.54%	99.55%	99.98%	99.98%	99.18%	99.94%	99.98%	99.98%	99.98%	99.98%	99.98%
Total Average		99.6%	99.3%	99.6%	99.5%	99.9%	99.8%	99.8%	98.1%	98.5%	97.7%	99.0%	98.7%	99.3%

BDL = Below detection limit (0.1 µg/L).

TABLE 3-6. REDUCTION IN HEADSPACE VOLATILE ORGANIC CONCENTRATIONS, BACHARACH TLV SNIFFER RESULTS

Sample No.	Run No.	Headspace concentration (ppm hexane)[a]	% Reduction in headspace concentration[b]
LUWA-43	Feed, 3rd drum	>10,000	
LUWA-44	Feed, 3rd drum	>10,000	
LUWA-81	Feed, 4th Drum	>10,000	
LUWA-82	Feed, 4th Drum	>10,000	
LUWA-106	Feed, 5th Drum	>10,000	
LUWA-107	Feed, 5th Drum	>10,000	
LUWA-47	5	82	
LUWA-65	5	78	
LUWA-66	5	81	
	Run 5 average	80	99.2
LUWA-50	6	98	99.0
LUWA-56	7	120	
LUWA-57	7	120	
	Run 7 average	120	98.8
LUWA-75	8	83	
LUWA-76	8	72	
	Run 8 average	78	99.2
LUWA-87	9	32	99.7
LUWA-93	10	32	
LUWA-94	10	23	
	Run 10 average	28	99.7
LUWA-103	11	200	98.0
LUWA-110	12	69	99.3
LUWA-113	13	60	99.4
LUWA-116	14	20	99.8
LUWA-119	15	52	99.5
LUWA-122	16	55	99.5
LUWA-125	17	40	99.6
LUWA-128	18	100	99.0

[a]Measurements taken at 25 °C.

[b]This calculation used the maximum range of the Bacharach TLV sniffer, 10,000 ppm, this percent removal is a minimum percent reduction in headspace volatile organic compounds; the actual percent reduction would be higher.

TABLE 3-7. VOLATILE ANALYSIS OF LIQUID AND SLUDGE PROCESS SAMPLES (COMPUCHEM DATA)

LUWA run #			5	5	7	7	8	8	10	10	10
Sample number	LUWA-185	LUWA-188	LUWA-68	LUWA-149	LUWA-59	LUWA-156	LUWA-78	LUWA-164	LUWA-96	LUWA-172	LUWA-168
Sample type	feed, mg/kg	feed, mg/kg	bottoms, mg/kg	org cond, mg/kg	bottoms, mg/kg	org cond, mg/kg	bottoms, mg/kg	org cond, mg/kg	bottoms mg/kg	org cond, mg/kg	aq cond, mg/kg
Sample prep/analytical	a	a	a	b	a	b	a	b	a	b	c
Compounds											
Benzene	230	0.2	0.97	4,500	BDL	6,000	0.64	1,300	0.56	1,900	1.4
2-Hexanone				1,800							
Toluene	2,800	1	5.8	85,000	6.1	120,000	4.6	25,000	2.7	34,000	4.6
Ethylbenzene	180	0.175	0.7	6,500	2.1	7,800	0.58	2,000	0.39	24,000	0.16
Styrene	160	0.39	0.84	3,700	2.5	5,000	1.6	BDL	1.2	1,300	0.15
m-Xylene	280	d	1.3	7,000	3.8	9,700	0.93	2,200	0.71	2,800	0.21
o,p-Xylene	280	d	1.4	12,000	4.4	14,600	0.9	3,800	0.72	4,900	0.2
Surrogate recovery											
D4-1,2-Dichloroethane	68	100	86	e	99	e	77	e	77	e	97
Bromofluorobenzene	102	95	79	e	78	e	69	e	69	e	97
D8-Toluene	86	86	81	e	96	e	68	e	68	e	104

[a]Extraction of 4 g of sample (nominal weight) with 10 mL methanol, GC/MS.
[b]Dilution of samples 1:1000 with methanol, GC/MS.
[c]Purge and trap of 175 µL sample, GC/MS.
[d]Xylenes obscured by high background of other chemicals, xylenes may be present.
[e]Surrogate measurement not possible due to large sample dilution required the analysis of the prepared sample.

Table 3-8 lists the semivolatile analysis for the same set of samples. The agreement between the two feed samples is much better for this analysis and reflects the separate preparation of samples for analysis in the two procedures. The aqueous condensate again showed relatively low concentrations of semivolatiles relative to the organic condensates, although several additional components were identified in the aqueous condensate that were not identified elsewhere. A metals analysis of the feeds, one bottoms sample, and one organic condensate sample was also performed. These results are listed in Table 3-9. This analysis was performed primarily for feed characterization and to demonstrate where metals entering with the feed appeared. Only small amounts of toxic metals were detected in the organic condensate, except for arsenic, which was present at 0.128 ppm.

Tables 3-10, 3-11, 3-12, and 3-13 compile the volatile and semivolatile results for runs 5, 7, 8, and 10. Percent removal from the feed sludge, percent reduction in concentration between the feed and bottoms, and mass balance closures are calculated for each component identified. The volatile removal from the feed sludge was 99.5+ percent for all volatiles in runs 5, 8 and 10. Runs 8 and 10 showed 99.9+ percent removal for all volatiles measured. The removal of volatiles for run 7 was slightly lower (98.6+ percent), which is attributable to the relatively low temperature of operation (150 °C) and high feed rate (154 lb/h) for this run. The concentrations of heavier semivolatile compounds were increased in the bottoms for runs 8 and 9. This would be caused principally by the removal of the volatile material in the feed, increasing the apparent concentration of these compounds.

The observed mass balance closures are somewhat disconcerting in that there is a substantial bias toward more material flowing into the process than is leaving (runs 5, 8, and 10). The volatile components show better closure than the semivolatile components. The closures for run 7 are much better, however, where closure is within about 25 percent. There are two reasonable explanations for this. First, the semivolatiles may be thermally changed or cross-linked as they pass through the TFE into larger, unanalyzable molecules, showing loss of the components while also preventing closure of the mass balance. Second, the bottoms may not have extracted as well as the feed samples, reducing the amount of the components extracted from the bottoms and producing a low analysis for the bottoms samples. The bottoms from run 7 (which showed the best mass balance closure) resembled the feed substantially. Very little material was evaporated from the feed during this run, and the temperature was relatively low (150 °C). Its components would have undergone the least change as a result of processing, and it would be nearly as extractable as the original feed. The almost identical percent removal from feed and mass balance closures for benzo(a)anthracene, chrysene, benzo(b)flouranthene, benzo(k)flouranthene, and benzo(a)pyrene in runs 5, 7, and 10 show that these materials are not actually removed from the feed; rather, they are bound to the bottoms samples to reduce their apparent concentrations in the analyzed samples.

The flow rate of gases from the condenser vent were also measured during the testing of the TFE. Table 3-14 lists the measurements of vent gas flow and concentrations for each of the runs. The vapor hydrocarbon concentrations above the bottoms samples as they were removed from the TFE are also listed in

TABLE 3-8. SEMIVOLATILE ANALYSIS OF LIQUID AND SLUDGE PROCESS SAMPLES (COMPUCHEM DATA)

LUWA run # Sample number Sample type	5 LUWA-185 feed, mg/kg	5 LUWA-188 feed, mg/kg	5 LUWA-68 bottoms, mg/kg	5 LUWA-149 org cond, mg/kg	7 LUWA-59 bottoms, mg/kg	7 LUWA-156 org cond, mg/kg	8 LUWA-78 bottoms, mg/kg	8 LUWA-164 org cond, mg/kg	10 LUWA-96 bottoms, mg/kg	10 LUWA-172 org cond, mg/kg	10 LUWA-168 aq cond, mg/kg
Sample prep/analytical	a	a	a	b	a	b	a	b	a	b	c
Compounds											
Phenol											0.21
Benzyl alcohol											0.098
2-Methylphenol											0.55
4-Methylphenol											0.41
2,4-Dimethylphenol											0.17
Bis(2-ethylhexyl) phthalate											0.022
Naphthalene	650	880	160	7,000	520	5,000	46	5,000	24	5,400	1.4
2-Methylnaphthalene	790	BDL	320	5,000	660	3,000	120	6,000	99	6,000	0.74
Acenaphthylene	BDL	21	8.2	BDL	BDL	BDL	11	160	14	190	BDL
Acenaphthene	47	BDL	15	110	BDL	BDL	BDL	240	BDL	300	BDL
Dibenzofuran	31	43	19	75	26	BDL	20	240	30	260	BDL
Fluorene	77	94	40	125	54	63	62	500	89	580	0.1
n-Nitrosodiphenylamine				120							
Phenanthrene	180	270	120	55	200	40	220	800	430	750	0.096
Anthracene	17	23	17	BDL	18	BDL	28	70	430	54	BDL
Pyrene	36	45	14	BDL	24	BDL	54	95	80	60	BDL
Benzo(a)anthracene	20	18	9.6	BDL	22	BDL	36	BDL	38	BDL	BDL
Chrysene	28	36	17	BDL	31	BDL	70	BDL	86	BDL	BDL
Di-N-Octyl phthalate		35									
Benzo(b)fluoranthene (f)	11	15	6.9	BDL	13	BDL	44	BDL	49	BDL	BDL
Benzo(k)fluoranthene (f)	11	15	6.9	BDL	13	BDL	44	BDL	49	BDL	BDL
Benzo(a)pyrene	BDL	14	7.7	BDL	12	BDL	28	BDL	31	BDL	BDL
Surrogate recovery											
2-Fluorophenol	d	d	d	e	d	e	d	e	d	e	59
D5-Phenol											47
D5-Nitrobenzene											87
2-Fluorobenzene											84
2,4,6-Tribromophenol											88
D14-Terphenyl											93
D10-Pyrene											92

BDL = Below detection limit; this limit varies with the sample analyzed, due to differences in sample preparation and dilution prior to analysis; limits can be found with the results reported in Appendix F.

[a]30 g (nominal) samples extracted with methylene chloride, final extract Volume 8-10 mL, GC/MS.
[b]1.0 g oil diluted to 25 mL with methylene chloride, GC/MS.
[c]100 mL of sample extracted with methylene chloride at pH >11 and pH <2, extract concentrated to 1.0 mL, GC/MS.
[d]Sample was diluted for analysis, surrogates below detection limits.
[e]Surrogates were not added to diluted oil samples.
[f]Co-eluting isomers.

TABLE 3-9. METALS ANALYSIS OF LIQUID AND SLUDGE PROCESS SAMPLES (COMPUCHEM DATA)

LUWA run # Sample number Sample type	Method used	LUWA-185 feed, ppm	LUWA-188 feed, ppm	10 LUWA-96 bottoms, ppm	10 LUWA-172 org cond, ppm
Aluminum	ICP	1,470	2,060	1,590	0.034
Arsenic	ICP	1.7	1.1	1.2	0.128
Barium	Furnace	21	29	33	
Calcium	ICP	1,360	1,610	2,540	0.173
Chromium	ICP	27	28	55	
Cobalt	ICP	2.9	2	3.4	
Copper	ICP	48	62	95	
Iron	ICP	1,370	1,750	2,210	0.065
Lead	ICP	58	72	105	0.005
Magnesium	ICP	317	352	816	
Manganese	ICP	17	19	30	
Nickel	ICP	9.8	14	16	
Sodium	ICP	349	399	1,200	
Vanadium	ICP	3.1	3.1	3.5	
Zinc	ICP	92	111	179	0.013

The following metals were below the detection limits for all samples:

Antimony	ICP
Beryllium	ICP
Cadmium	ICP
Mercury	CV
Potassium	AA
Selenium	Furnace
Silver	ICP
Thallium	Furnace

ICP = inductively coupled plasma
Furnace = furnace atomic absorption
AA = flame atomic absorption.

TABLE 3-10. PERFORMANCE OF THIN-FILM EVAPORATOR, VOLATILE AND SEMIVOLATILE COMPOUNDS, RUN #5

Run #5	Feed[a]	Bottoms	Aqueous condensate	Organic condensate	% Removal from feed[b]	% Reduction in concentration from feed[c]	Mass balance closure[d] (% difference)
Feed rates (lb/h)	71.6	55.2	14.66	1.74			
Concentrations	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)			
Benzene	230	0.97	e	4,500	99.67	99.58	52
2-Hexanone				1,800			
Toluene	2,800	5.8		85,000	99.84	99.79	26
Ethylbenzene	180	0.7		6,500	99.70	99.61	12
Styrene	160	0.84		3,700	99.60	99.48	43
m-Xylene	280	1.3		7,000	99.64	99.54	39
o,p-Xylene	280	1.4		12,000	99.61	99.50	-5
Naphthalene	765	160		7,000	83.88	79.08	62
2-Methylnaphthalene	790	320		5,000	68.77	59.49	53
Acenaphthylene	21	8.2		BDL	69.90	60.95	70
Acenaphthene	47	15		110	75.40	68.09	70
Dibenzofuran	37	19		75	60.41	48.65	55
Fluorene	85.5	40		125	63.93	53.22	60
n-Nitrosodiphenylamine				120			
Phenanthrene	225	120		55	58.88	46.67	58
Anthracene	20	17		BDL	34.47	15.00	34
Pyrene	40.5	14		BDL	73.35	65.43	73
Benzo(a)anthracene	19	9.6		BDL	61.05	49.47	61
Chrysene	32	17		BDL	59.04	46.88	59
Di-n-octyl phthalate	17.5						
Benzo(b)fluoranthene[f]	13	6.9		BDL	59.08	46.92	59
Benzo(k)fluoranthene[f]	13	6.9		BDL	59.08	46.92	59
Benzo(a)pyrene	14	7.7		BDL	57.60	45.00	58

BDL = Below detection limits.

[a]Feed concentrations used are a composite of the two semivolatile and volatile analyses.

[b]Calculated as (1 - bottoms rate x concentration/feed rate x concentration) x 100.

[c]Calculated as (feed concentration - bottoms concentration)/feed concentration x 100.

[d]((Feed-bottoms-organic condensate)/feed) x 100%.

[e]Condensate sample not analyzed for this run.

[f]Co-eluting isomers.

TABLE 3-11. PERFORMANCE OF THIN-FILM EVAPORATOR, VOLATILE AND SEMIVOLATILE COMPOUNDS, RUN #7

Run #7	Feed[a]	Bottoms	Aqueous condensate	Organic condensate	% Removal from feed[b]	% Reduction in concentration from feed[c]	Mass balance closure[d] (% difference)
Feed Rates (lb/h)	153.7	139	11.93	2.67			
Concentrations	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)			
Benzene	230	BDL	e	6,000	99.76[f]	99.73[f]	55
2-Hexanone							
Toluene	2,800	6.1		120,000	99.80	99.78	25
Ethylbenzene	180	2.1		7,800	98.94	98.83	24
Styrene	160	2.5		5,000	98.59	98.44	44
m-Xylene	280	3.8		9,700	98.77	98.64	39
o,p-Xylene	280	4.4		14,600	98.58	98.43	8
Naphthalene	765	520		5,000	38.53	32.03	27
2-Methylnaphthalene	790	660		3,000	24.45	16.46	18
Acenaphthylene	21	BDL		BDL			
Acenaphthene	47	BDL		BDL			
Dibenzofuran	37	26		BDL	36.45	29.73	36
Fluorene	85.5	54		63	42.88	36.84	42
Phenanthrene	225	200		40	19.61	11.11	19
Anthracene	20	18		BDL	18.61	10.00	19
Pyrene	40.5	24		BDL	46.41	40.74	46
Benzo(a)anthracene	19	22		BDL	-4.72	-15.79	-5
Chrysene	32	31		BDL	12.39	3.13	12
Di-n-octyl phthalate	17.5						
Benzo(b)fluoranthene[g]	13	13		BDL	9.56	0.00	10
Benzo(k)fluoranthene[g]	13	13		BDL	9.56	0.00	10
Benzo(a)pyrene	14	12		BDL	22.48	14.29	22

BDL = Below detection limits.

[a]Feed concentrations used are a composite of the two semivolatile and volatile analyses.

[b]Calculated as (1 - bottoms rate x concentration/feed rate x concentration) x 100.

[c]Calculated as (feed concentration - bottoms concentration)/feed concentration x 100.

[d]((Feed-bottoms-organic condensate)/feed) x 100%.

[e]Condensate sample not analyzed for this run.

[f]Uses reported detection limit of 0.62 mg/kg for benzene.

[g]Co-eluting isomers.

TABLE 3-12. PERFORMANCE OF THIN-FILM EVAPORATOR, VOLATILE AND SEMIVOLATILE COMPOUNDS, RUN #8

Run #8	Feed[a]	Bottoms	Aqueous condensate	Organic condensate	% Removal from feed[b]	% Reduction in concentration from feed[c]	Mass balance closure[d] (% difference)
Feed rates (lb/h)	68.5	8.5	53.22	6.78			
Concentrations	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)			
Benzene	230	0.64	e	1,300	99.97	99.72	44
2-Hexanone							
Toluene	2,800	4.6		25,000	99.98	99.84	12
Ethylbenzene	180	0.58		2,000	99.96	99.68	-10
Styrene	160	1.6		BDL	99.88	99.00	100
m-Xylene	280	0.93		2,200	99.96	99.67	22
o,p-Xylene	280	0.9		3,800	99.96	99.68	-34
Naphthalene	765	46		5,000	99.25	93.99	35
2-Methylnaphthalene	790	120		6,000	98.12	84.81	23
Acenaphthylene	21	11		160	93.50	47.62	18
Acenaphthene	47	BDL		240			49
Dibenzofuran	37	20		240	93.29	45.95	29
Fluorene	85.5	62		500	91.00	27.49	33
Phenanthrene	225	220		800	87.87	2.22	53
Anthracene	20	28		70	82.63	-40.00	48
Pyrene	40.5	54		95	83.45	-33.33	60
Benzo(a)anthracene	19	36		BDL	76.49	-89.47	76
Chrysene	32	70		BDL	72.86	-118.75	73
Di-n-octyl phthalate	17.5						
Benzo(b)fluoranthene[f]	13	44		BDL	58.00	-238.46	58
Benzo(k)fluoranthene[f]	13	44		BDL	58.00	-238.46	58
Benzo(a)pyrene	14	28		BDL	75.18	-100.00	75

BDL = Below detection limits.

[a]Feed concentrations used are a composite of the two semivolatile and volatile analyses.

[b]Calculated as (1 - bottoms rate x concentration/feed rate x concentration) x 100.

[c]Calculated as (feed concentration - bottoms concentration)/feed concentration x 100.

[d]((Feed-bottoms-organic condensate)/feed) x 100%.

[e]Condensate sample not analyzed for this run.

[f]Co-eluting isomers.

TABLE 3-13. PERFORMANCE OF THIN-FILM EVAPORATOR, VOLATILE AND SEMIVOLATILE COMPOUNDS, RUN #10

Run #10	Feed[a]	Bottoms	Aqueous condensate	Organic condensate	% Removal from feed[b]	% Reduction in concentration from feed[c]	Mass balance closure[d] (% difference)
Feed rates (lb/h)	143.4	18.6	111.93	12.87			
Concentrations	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)			
Benzene	230	0.56	1.4	1,900	99.97	99.76	25
2-Hexanone							
Toluene	2,800	2.7	4.6	34,000	99.99	99.90	-9
Ethylbenzene	180	0.39	0.16	24,000	99.97	99.78	-1097
Styrene	160	1.2	0.15	1,300	99.90	99.25	27
m-Xylene	260	0.71	0.21	2,800	99.97	99.75	10
o,p-Xylene	280	0.72	0.2	4,900	99.97	99.74	-57
Phenol			0.21				
Benzyl alcohol			0.056				
2-Methylphenol			0.55				
4-Methylphenol			0.41				
2,4-Dimethylphenol			0.17				
Bis(2-ethylhexyl) phthalate			0.022				
Naphthalene	765	24	1.4	5,400	99.59	96.86	36
2-Methylnaphthalene	790	99	0.74	6,000	98.37	87.47	36
Acenaphthylene	21	14	BDL	190	91.36	33.33	10
Acenaphthene	47	BDL	BDL	300			43
Dibenzofuran	37	30	BDL	260	89.48	18.92	26
Fluorene	85.5	89	0.1	580	88.58	-4.09	26
Phenanthrene	225	430	0.096	750	75.21	-91.11	45
Anthracene	28	430	BDL	54	-178.87	-2050.00	-283
Pyrene	40.5	80	BDL	60	74.38	-97.53	61
Benzo(a)anthracene	19	38	BDL	BDL	74.66	-100.00	74
Chrysene	32	86	BDL	BDL	66.14	-168.75	66
Di-n-octyl phthalate	17.5						
Benzo(b)fluoranthene[e]	13	49	BDL	BDL	61.11	-276.92	51
Benzo(k)fluoranthene[e]	13	49	BDL	BDL	61.11	-276.92	51
Benzo(a)pyrene	14	31	BDL	BDL	71.28	-121.43	71

BDL = Below detection limits.

[a]Feed concentrations used are a composite of the two semivolatile and volatile analyses.

[b]Calculated as (1 - bottoms rate x concentration/feed rate x concentration) x 100.

[c]Calculated as (feed concentration - bottoms concentration)/feed concentration x 100.

[d](Feed-bottoms-organic condensate-aqueous condensate/feed) x 100%.

[e]Co-eluting isomers.

TABLE 3-14. MEASUREMENTS OF VENT GAS FLOW RATE AND BACHARACH TLV SNIFFER MEASUREMENTS

Date	Run No.	Time	Location	Measurement[a]	Value
9/09/86	1	09:47	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	1		Condenser vent	Flow rate	<10 mL/min
9/09/86	2	10:05	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	2		Condenser vent	Flow rate	<10 mL/min
9/09/86	3	10:40	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	3		Condenser vent	Flow rate	<10 mL/min
9/09/86	5	13:19	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	5		Condenser vent	Flow rate	250 mL/min
9/09/86	5		Feed tank headspace	Total HC	>10,000 ppm Hexane
9/09/86	6	13:56	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	6		Condenser vent	Flow rate	250 mL/min
9/09/86	7	14:33	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/09/86	7		Condenser vent	Flow rate	200 mL/min
9/10/86	8	09:15	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	8		Condenser vent	Flow rate	15 mL/min
9/10/86	9	11:33	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	9		Condenser vent	Flow rate	16 mL/min
9/10/86	10	12:06	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	10		Condenser vent	Flow rate	<10 mL/min
9/10/86	11		Vacuum run, condenser flow could not be measured		
9/10/86	12	16:09	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	12		Condenser vent	Flow rate	<10 mL/min
9/10/86	13	16:45	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	13		Condenser vent	Flow rate	30 mL/min
9/10/86	14	17:35	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	14		Condenser vent	Flow rate	30 mL/min
9/10/86	15	18:00	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	15		Condenser vent	Flow rate	24 mL/min
9/10/86	15	18:09	Vapors above bottoms when removed from TFE	Total HC	110 ppm Hexane

(continued)

TABLE 3-14 (continued)

Date	Run No.	Time	Location	Measurement	Value
9/10/86	16	18:28	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/10/86	16		Condenser vent	Flow rate	<10 mL/min
9/10/86	16		Vapors above bottoms when removed from TFE	Total HC	200 ppm Hexane
9/10/86	17	19:46	Vacuum run, condenser	flow could not be measured	
9/10/86	17		Vapors above bottoms when removed from TFE	Total HC	170 ppm Hexane
9/10/86	18	20:44	Vacuum run, condenser	flow could not be measured	
9/10/86	18		Vapors above bottoms when removed from TFE	Total HC	200 ppm Hexane
9/11/86	19	09:40	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/11/86	19		Condenser vent	Flow rate	9 L/min
9/11/86	19		Vapors above bottoms when removed from TFE	Total HC	250 ppm Hexane
9/11/86	20	10:50	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/11/86	20		Condenser vent	Flow rate	10.3 L/min
9/11/86	20		Vapors above bottoms when removed from TFE	Total HC	200 ppm Hexane
9/11/86	22	13:15	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/11/86	22		Condenser vent	Flow rate	2.4 L/min
9/11/86	22		Vapors above bottoms when removed from TFE	Total HC	190 ppm Hexane
9/11/86	21	13:35	S4, Cond vent	Total HC	>10,000 ppm Hexane
9/11/86	21		Condenser vent	Flow rate	0.75 L/min
9/11/86	21		Vapors above bottoms when removed from TFE	Total HC	700 ppm Hexane

[a]HC = Hydrocarbon as measured with Bacharach TLV Sniffer.

this table. All of the condenser vent gas concentrations exceeded the range of the Bacharach TLV meter used for this measurement. The flow rates from the condenser were highly dependent upon the waste being processed in the TFE. The emulsion tank sludge showed only minimal flows from the condenser vent, with a maximum of 250 mL/min being recorded during runs 5 and 6. The second waste sample, however, showed much higher rates of vapor flow from the condenser. Flows of 9 and 10 L/min were measured during runs 19 and 20. Because any TFE used for waste processing would probably handle a wide variety of wastes from the plant environment, and many of these wastes would be expected to have substantial amounts of light hydrocarbons that would not condense at process cooling water temperatures, either a glycol-cooled condenser or a two-stage condenser (first-stage cooling water, second-stage chilled glycol) should be employed. As an alternative, the condenser vent gas could be routed to either an incineration system or flare to destroy any uncondensed hydrocarbons.

Tables 3-15 and 3-16 show the results from measurements of vent gas concentrations. These samples were taken in evacuated canisters and analyzed by GC and GC/MS. Table 3-15 has the results of GC analysis of these samples, where the measured peak areas were grouped according to the number of carbon atoms in each compound (for compounds containing 1 through 6 carbon atoms). GC/MS analyses of one gas sample canister and the headspace of two feed samples are listed in Table 3-16. The feed headspace analysis was used in identifying components found in the onsite GC analysis of sample headspace (Table 3-5).

The results of an oil, water, and solids analysis are listed in Table 3-17. The residue analysis for solids was a slightly modified Method 224G (Standard Methods for the Analysis of Water and Wastewater). Exactly 25 g of each sample were placed into weighing dishes, dried at 105 °C for 1 hour, cooled in a desiccator, weighed, dried at 300 °C for 1 hour, cooled in a desiccator, weighed, and then ashed at 550 °C for 1 hour. The weights after each drying were recorded, and the residue after drying at each temperature recorded. This analysis was performed principally to determine the solids of the samples, but the weight loss at 105 °C corresponds to the loss of water and volatiles, heavier oils are lost between 105 and 300 °C, and the final residue after ashing represents the inorganic material of the samples.

The oil was analyzed by extraction of the samples with freon, followed by spectrophotometric measurement of the oil (Method 413.2). Water content of samples was determined by Carl-Fischer titration. These results do not appear very good in that the feeds and bottoms show very high water contents and very high oil contents. It would be impossible to have samples with both 880 to 950 g/L of oil and water contents between 59 and 63 percent. The very high oil contents measured indicate that the freon extraction technique was inappropriate for the analysis of sample oil content. Several valid points can be made from these data, however. There was very little oil in the aqueous condensate and very little water in the oil, indicating very clean splits between the oil and aqueous condensates. The solids and heavy oil contents of the bottoms from runs 8 and 10 were increased substantially from their feed concentrations.

TABLE 3-15. VENT GAS CONCENTRATIONS

Run No.	Sample No.	C1 Range (ppm)	C2 Range (ppm)	C3 Range (ppm)	C4 Range (ppm)	C5 Range (ppm)	C6 Range (ppm)
5	LUWA-70				84	3,100	6,900
7	LUWA-62			340	130	3,800	3,800
7	LUWA-61			470	520	7,700	7,700
8	LUWA=84		210	650	640	6,500	4,200
8	LUWA-85		28	43		100	1,100
10	LUWA-99		92	130	200	4,000	4,200

TABLE 3-16. GC/MS ANALYSIS OF GAS SAMPLES, VENT GAS, AND HEADSPACE (IEA)

Compound	Vent gas run #10 LUWA-98, µg/L	Vent gas run #10 LUWA-98, µg/L	Average vent gas run #10, µg/L	% Difference vent gas run #10	Feed headspace drum #3 LUWA-44, µg/L	Feed headspace drum #4 LUWA-81, µg/L
2-Methyl propane						1,800
Butane	2,800	2,600	2,700	7	2,200	3,800
2-Butene					890	1,400
Cyclopentane					870	1,000
2-Methyl butane	6,000	4,800	5,400	22	4,500	6,300
Pentane	8,800	6,800	7,800	26	6,300	8,300
2-Methyl-1-pentene		1,200				
Methyl cyclopentane	2,300	1,700	2,000	30	1,600	1,900
3-Methyl pentane	2,500	1,800	2,150	33		
2-Methyl pentane	6,300	4,400	5,350	36	4,300	5,000
Benzene	3,000	2,000	2,500	40	1,800	2,000
Hexane	3,900	2,500	3,200	44	2,300	2,600
Methyl cyclohexane	1,500	1,000	1,250	40	1,000	
3-Methyl hexane	1,400					
Toluene	10,000	7,200	8,600	33	7,600	8,000
Ethyl benzene	878					
m-Xylene	106					

TABLE 3-17. OIL, WATER, AND SOLIDS ANALYSIS OF PROCESS STREAMS FOR RUNS 5, 7, 8, AND 10[a]

	Feed drum #3 LUWA-45	Feed drum #4 LUWA-83	Feed drum #4 LUWA-83D	Run #5 bottoms LUWA-69	Run #5 aq cond LUWA-145	Run #6 org cond LUWA-150	Run #7 bottoms LUWA-60	Run #7 aq cond LUWA-152	Run #7 org cond LUWA-157	Run #8 bottoms LUWA-79	Run #10 bottoms LUWA-97	Run #10 aq cond LUWA-169	Run #10 org cond LUWA-173
Solids													
Residue 105 °C	34.8%	36.6%	34.4%	16.7%			42.6%			86.6%	89.3%	0.07%	45.1
Residue 300 °C	2.8%	3.4%	5.7%	2.1%			3.3%			26.9%	18.9%	0.06%	0.0
Residue 550 °C	0.1% [2.1%]	1.8% [2.6%]	1.0% [2.3%]	0.9% [2.84%]			1.6% [3.04%]			7.3% [12.44%]	4.6% [13.14%]	0.04%	0.0
Oil (g/L)	880 [16.6%]	860 [21.96%]	840 [24.7%]	960 [20.11%]	<.02 [0.1%]		730 [23.66%]	<.02 [0.1%]		950 [75.5%]	1000 [81.65%]		810
Water (weight %)	71.00% [81.3%]	59.00% [74.8%]	59.00% [73.0%]	63.00% [77.06%]		0.04%	47.00% [73.28%]		0.02%	8.70% [20.44%]	1.70% [5.16%]		0.40

[a]Numbers in block parentheses are the values reported by Chevron research (see Appendix I).

PROCESS RESIDUALS

Bottoms Sludge

The bottoms sludge from the TFE was very similar to the feed for the low-temperature runs. The only difference between the feed and bottoms for these runs was the removal of most of the volatile organics and some of the water from the original feed. Any disposal methods employed for the original feed should be successful with the bottoms from the low-temperature runs. The feed from the high-temperature runs was substantially more viscous and had a much higher solids content than the original feed. Most of the water, volatile organics, and oils had been removed by the processing of the feed sludge. This material could probably be incinerated successfully or disposed of by other methods currently used for the raw feed sludge. This material may be somewhat less biodegradable since most of the organics remaining in the bottoms are relatively heavy oils.

The bottoms from the high-temperature vacuum run were even more viscous than the other bottoms and had much more of the oils removed from the bottoms when compared visually to other samples. In this form, the volume of waste for disposal was substantially reduced, but it may present some additional disposal problems because of its tarry and viscous nature.

Organic Condensate

The organic condensate is a potentially useful effluent stream from the treatment process. The organic condensate from the low-temperature runs was an organic oil with a very high concentration of volatiles. It was very clean, had very little solids, and had only a slight color. This organic condensate could easily be recycled to numerous raw product streams within a refinery and would be an economic credit to the process operation. The organic condensates from the high-temperature runs were very similar to product from lower temperature runs, but contained more of the heavier boiling oils. It had more of a caramel color, a heavier burned organic odor, but could still be recycled as a raw product to the refinery operations. The organic condensate is the most valuable recovered material from the process and its reuse within the refinery will reduce the overall cost of the waste treatment.

Organic condensates produced during the vacuum runs were in the form of an organic/water emulsion. The emulsion from the high-temperature vacuum run (run 11) never completely separated, even when left standing for a substantial period of time. The emulsions from the low-temperature vacuum runs (runs 17 and 18) separated more substantially, but might require larger separations tanks in installed systems. A two-stage system where the water and volatile organics are removed in the first TFE (at atmospheric pressure) and the heavier organics are removed in a second TFE (under vacuum) would remove the emulsion problems while producing two different organic fractions for recycling to refinery operations.

Aqueous Condensate

There are several methods available for the treatment of the aqueous condensate. When only a relatively small amount of the total water in the feed waste is recovered as condensate (as in runs 5, 6, and 7), the aqueous condensate stream could be recycled to the TFE feed stream. This would increase the inlet water percentage to the evaporator, and all water would eventually exit with process bottoms for normal disposal of the bottoms sludge. This would be appropriate for the removal of volatiles only from the waste sludges, but would not work when either dewatering of the waste or recovery of lower boiling oils from the feed is desired. Another rather easy method of handling the aqueous condensate would be to send it to an API separator, where it would be combined with other oil-contaminated water streams for treatment.

COST OF THIN-FILM EVAPORATION

Results from the pilot-scale TFE test were used to select two possible modes of operation upon which a cost estimation was made.

In the first mode, the evaporator is operated under relatively mild conditions, with a low heating temperature (150 °C) and high feed rates. Almost all of the volatiles and some of the water are removed under these conditions, but the bottoms produced are only slightly changed from the initial feed. These conditions correspond to run #7 of the pilot-scale tests and remove the volatiles from the waste prior to ultimate disposal without requiring the evaporation of all the water in the sludge. The second possible application uses a higher drum temperature (310 °C) to evaporate essentially all of the volatiles and water from the waste and to recover much of the higher boiling oils. This second mode of operation corresponds to run #10 of the pilot-scale tests. These conditions substantially reduce the amount of waste sludge for ultimate disposal and recover much more of the hydrocarbon oils in the original waste. The additional recovered oils are an economic credit to the process cost, but additional energy is expended in the process and heated oil is required instead of steam to heat the process.

A wide range of TFE sizes is also possible. The installed unit size will be determined by the amount of sludge to be processed at any given site. Two different sized units are examined here, one with 53.8 ft^2 of heat transfer area and the other with 258.2 ft^2 of heated area. The cost of these two sizes of TFEs was obtained from Luwa Corporation along with an estimate of the other costs associated with TFE operation.

An estimate of the cost of refinery waste treatment using a TFE was made. The estimate includes the land disposal costs for the TFE bottoms, water treatment costs for the aqueous condensate, and a credit for the recovered organic condensate. Table 3-18 presents the results of the cost estimate for refinery waste treatment based on the different modes of TFE operation. The cost of TFE treatment is compared with the cost of disposing the same wastes by landfarming ($100/ton).

TABLE 3-18. TFE COST ESTIMATION

	TFE modes of operation			
	A	B	C	D
TFE size (ft^2)	53.8	53.8	258.2	258.2
Operating temperature (°C)	150	310	150	310
Feed rate (lb/hr)	2,690	2,690	12,910	12,910
Product flow rates (% of feed)				
Oil	1.7	9.0	1.7	9.0
Water	7.8	78.1	7.8	78.1
Bottoms	90.5	12.9	90.5	12.9
Treatment cost ($/ton)[a]	116	37	89	25
Difference from landfarming (%)	+16.1	-63.1	-11.4	-74.9

[a]Cost includes utilities, labor, maintenance, taxes, insurance, disposal of bottoms, and capital recovery. The cost of disposal of bottoms is the major component of total cost.

SECTION 4

FIELD TEST RESULTS: STEAM STRIPPING

RESULTS FOR PLANT I

Process Description for Plant I

Plant I produces mono-carbon chlorinated solvents such as methylene chloride, chloroform, and carbon tetrachloride. A steam stripper is used to recover solvents and to treat the plant's wastewater. The major contaminants that are removed and monitored by the plant include methylene chloride, carbon tetrachloride, and chloroform with National Pollutant Discharge Elimination System (NPDES) discharge limits of 50, 55, and 75 parts per billion (ppb), respectively. Plant analyses showed that the concentrations in the effluent were generally on the order of 50 to 75 percent of the limits given above. Concentrations in the feed stream to the steam stripper are quite variable and range from hundreds of parts per million to saturation of the water phase with organics.

The wastewater at this plant consists of equipment wash water and rainfall collected from diked areas around the plant; consequently, the flow rate and composition of the wastewater is cyclical and dependent on the amount of rain. Plant personnel indicated that the steam stripper operated roughly 75 percent of the time with accumulation in storage when the stripper is not operating. Once the stripper is started, it operates in an essentially continuous mode until the wastewater in storage has been steam stripped.

A flow schematic of the treatment system is given in Figure 4-1. The wastewater enters one of the two decanters (each approximately 75,000 L or 20,000 gal) where it is processed as a batch. Sodium hydroxide solution (caustic) is added to the decanter to adjust the pH to the target of 7, and flocculants are added to aid in solids removal. The mixture is recirculated and mixed in the decanter and allowed to settle. The wastewater (upper layer) is sent to the stripper feed (or storage) tank (approximately 473,000 L or 125,000 gal). The organic layer (on the bottom) is removed periodically from the decanter and sent to a surge or collection tank, and solids are removed periodically with a vacuum truck for disposal. The cycle time of a batch of wastewater in the decanter is about 1 day. Approximately 15,000 L (4,000 gal) of sludge is generated each month and is disposed of offsite, usually by incineration.

The steam stripper is started after a sufficient quantity of water has accumulated in the storage tank. The stripper feed passes through a heat exchanger for preheating by the effluent from the stripper. The stripper column is packed with 2.5-cm (1-inch) saddles and processes about 41.6 L/min (11 gal/min). The stripper effluent, after cooling by the heat exchanger,

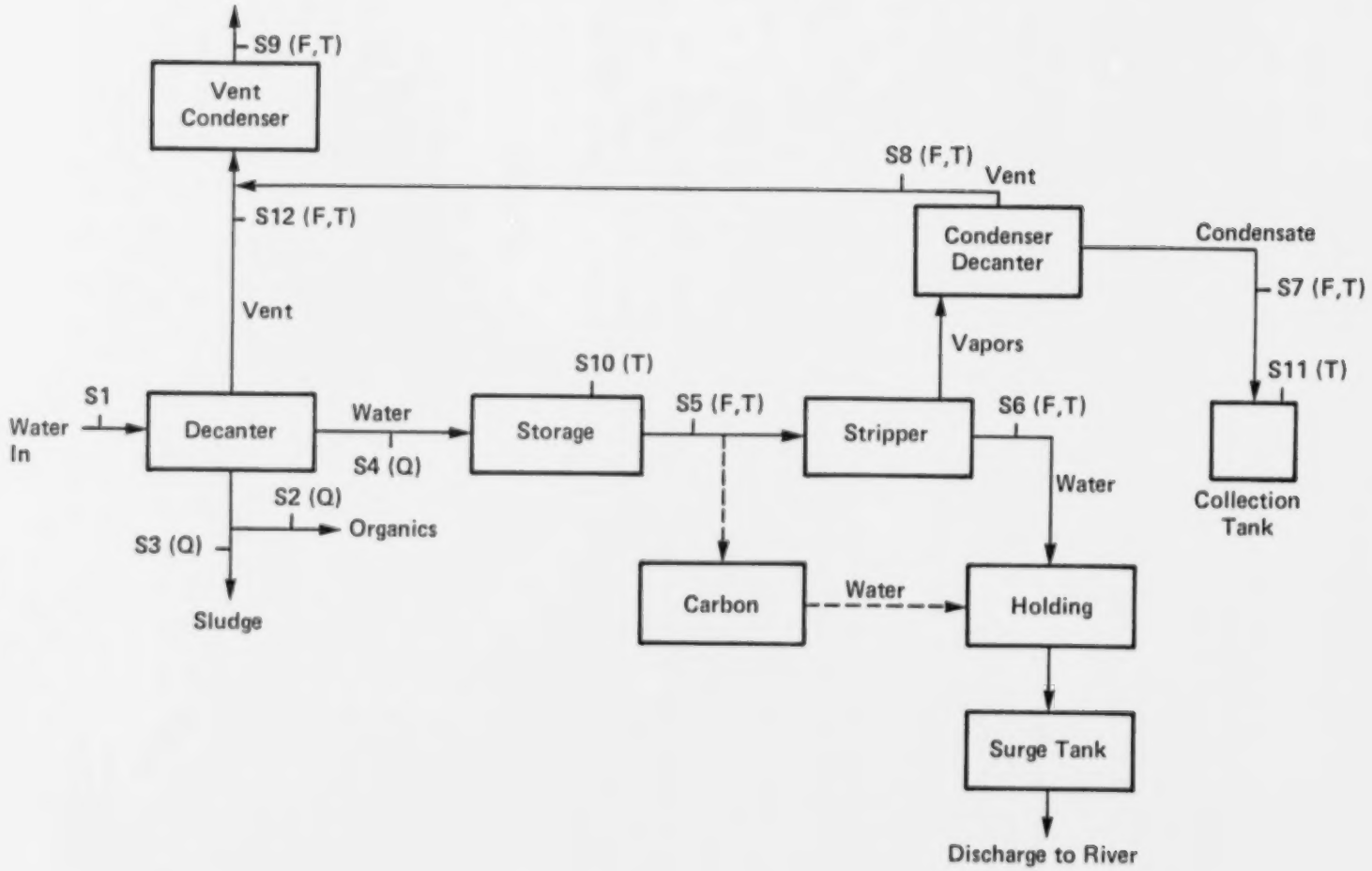

Figure 4-1. Simplified schematic of sampling points.
(S = sampling point, F = flowrate, T = temperature, Q = quantity)

enters one of two open-topped holding tanks (about 19,000 L or 5,000 gal) where it is analyzed for comparison with the discharge limits. If the analysis is satisfactory, the water is pumped to a surge tank where the pH is adjusted for final discharge to the river under the NPDES permit. If the analysis is not satisfactory, the water is treated again, either in the steam stripper or carbon adsorber (described below).

The overhead vapors from the stripper pass through a condenser cooled with cooling tower water. The condensate enters a decanter that separates the heavier organic layer from water. The entire water layer is returned to the steam stripper, and the organic layer is drained periodically by the operator to a small collection tank for recycle back to the process. The collection tank is open-topped and has a layer of water and sludge floating on top of the organic layer.

The condenser is vented through the decanter to a vent condenser (cooled with cooling tower water), as shown in Figure 4-1. The vent condenser receives vapors from the initial water/organics/solids decanters and the steam stripper condenser/decanter. The initial decanters and storage tank are fixed roof tanks and have conservation vents that open as necessary to prevent pressure buildup.

The plant also has two liquid phase carbon adsorbers operated in series with about 3,800 L (1,000 gal) of carbon in each (see the dashed lines in Figure 4-1). This system is used rarely and was installed as a backup unit in the event the stripper is down or if the capacity of the stripper is exceeded. When the carbon adsorber is used, the wastewater is pumped from the storage tanks through the adsorbers and into the holding tanks prior to analysis.

The original process schematic was claimed to be confidential information and was replaced by the more general block diagram in Figure 4-1. Similarly, the basic design information on the process was provided to EPA and is not given here because it was claimed to be confidential business information.

VO Removal From Water

A primary focus of the sampling effort was the assessment of VO removal from water for the steam stripper. The concentrations of individual VO constituents entering the stripper with the feed and leaving with the stripper bottoms are summarized for both test days in Tables 4-1 and 4-2. Methylene chloride and chloroform are the major constituents in the feed. Compounds detected at lower levels in the feed included chloromethane, carbon tetrachloride, trichloroethylene, and 1,1,2-trichloroethane. The concentrations for both test days are averaged in Table 4-3 and show that an average VO concentration in the feed of 5,858 ppm (0.6 percent) is reduced to less than 0.037 ppm in the stripper bottoms. The only compounds detected in the stripper bottoms were methylene chloride (7 of 11 runs), chloroform (4 of 11 runs), and carbon tetrachloride (1 of 11 runs) with detection limits of 0.005 ppm.

The only other compound detected in the feed and bottoms was 1,1-dichloroethane during Run 2-1, with a feed concentration of 4.7 ppm and a

TABLE 4-1. STRIPPER FEED (IN) AND BOTTOMS (OUT) CONCENTRATIONS FOR FIRST TEST DAY (ppm)

Compound	Run 1-1		Run 1-2		Run 1-3		Run 1-4		Run 1-5	
	In	Out	In	Out	In	Out	In	Out	In	Out
Chloromethane	31.1	<0.005	37.2	<0.005	47.6	<0.005	37.6	<0.005	35.7	<0.005
Methylene chloride	6,788	0.0116	4,893	0.017	4,077	0.013	4,760	0.009	4,951	<0.005
Chloroform	2,829	0.009	928	0.009	1,250	0.008	864	0.008	868	<0.005
Carbon tetrachloride	65.2	<0.005	51.2	0.008	67.2	<0.005	40.0	<0.005	48.8	<0.005
Trichloroethylene	10.7	<0.005	3.71	<0.005	--	<0.005	--	<0.005	--	<0.005
1,1,2-Trichloroethane	8.0	<0.005	4.98	<0.005	8.17	<0.005	4.35	<0.005	5.0	<0.005

TABLE 4-2. STRIPPER FEED (IN) AND BOTTOMS (OUT) CONCENTRATIONS FOR SECOND TEST DAY (ppm)

Compound	Run 2-1		Run 2-2		Run 2-3		Run 2-4		Run 2-5		Run 2-6	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Chloromethane	25.3	<0.005	32.3	<0.005	29.0	<0.005	28.0	<0.005	33.1	<0.005	21.5	<0.005
Methylene chloride	3,539	0.017	5,255	<0.005	3,471	<0.005	3,500	<0.005	4,746	0.007	3,419	0.023
Chloroform	1,316	<0.005	963	<0.005	1,200	<0.005	1,144	<0.005	1,353	<0.005	1,207	<0.005
Carbon tetrachloride	58.3	<0.005	48.7	0.005	60.8	<0.005	53.4	<0.005	52.2	<0.005	57.0	<0.005
Trichloroethylene	5.46	<0.005	3.9	<0.005	--	<0.005	--	<0.005	6.2	<0.005	3.7	<0.005
1,1,2-Trichloroethane	--	<0.005	--	<0.005	--	<0.005	--	<0.005	3.9	<0.005	2.6	<0.005

TABLE 4-3. SUMMARY OF FEED AND BOTTOMS CONCENTRATIONS (ppm)

Compound	Average in	Range	Average out	Range
Chloromethane	32.6	21.5-47.6	<0.005	--
Methylene chloride	4,490	3,419-6,788	0.011	<0.005-0.125
Chloroform	1,270	864-2,829	0.006	<0.005-0.009
Carbon tetrachloride	54.8	40-67	0.005	<0.005-0.008
Trichloroethylene	5.6	ND-10.7	<0.005	--
1,1,2-Trichloroethane	5.3	ND-8.2	<0.005	--
Total VO	5,858		<0.037	

bottoms concentration of 0.011 ppm. No 1,1-dichloroethane was detected in any of the other 10 samples of the feed or bottoms.

The stripper feed and bottoms also were evaluated for extractable organic compounds. The only extractable compound found was hexachloroethane at a level of 0.1 ppm in the feed and not detected (<0.01 ppm) in the bottoms. Because of the expense of analysis for extractable organics relative to the minor information obtained (i.e., low concentrations), no additional samples were analyzed for extractable organic content.

Removal efficiencies from water are given in Tables 4-4 and 4-5 for the two test days. The removal of the two major compounds, methylene chloride and chloroform, averaged over 99.999 percent. The removal of methylene chloride ranged from 99.996 to >99.9999 percent, and the removal of chloroform ranged from 99.998 to >99.9996 percent. The number of nines (9's) in the removal efficiency for the other compounds was determined by the feed concentration and detection limit values for the bottoms. The removal efficiency of these other compounds was over 99.8 percent. The overall VO removal efficiency, based on an average feed concentration of 5,858 ppm and an average bottoms concentration of less than 0.037 ppm, was approximately 99.999 percent.

Air Emissions

The flow rates and concentrations of VO in the vapor phase were determined at the primary condenser (S8), at the secondary vent condenser (S9), at the storage (or feed) tank vent (S10), and the solids decanter vent (S12). Headspace samples were taken from the open-top tank used as a surge or pumping tank for the organic condensate (S11).

The results of the vapor-phase sampling and analysis are given in Table 4-6. The major component of the vapors from the two condensers (S8 and S9) is methylene chloride at about 40 percent (by volume or total number of moles), followed by chloroform (roughly 4 percent), chloromethane (0.5 percent), and carbon tetrachloride (0.2 percent). Methylene chloride was also the dominant compound found in the storage tank vapor (S10) and in the vapor from the solids decanter (S12). The lowest vapor-phase concentrations were found over the open-top collection tank (S11), which had a layer of water and sludge floating on top of the organic layer and was exposed to the atmosphere.

The first sample taken from the storage tank vent (S10) at 11:10 yielded concentration results that were roughly a factor of 10 lower than the results from the other five samples. This set of results was evaluated by following the procedures outlined in Grubbs (Reference 1) to test for outliers. The statistical test suggested that the results for the sample taken at 11:10 are outliers at the 99-percent significance level. Similarly, the carbon tetrachloride result for the sample from the secondary condenser vent (S9) at 12:54 (0.57 percent) was found to be an outlier at the 99-percent significance level.

The vapor-phase concentrations from the two condensers are compared in Table 4-7. The two sets of average concentrations are very similar and are

TABLE 4-4. REMOVAL EFFICIENCY FROM WATER FOR FIRST TEST DAY (PERCENT)

Compound	Run 1-1	Run 1-2	Run 1-3	Run 1-4	Run 1-5	Average
Chloromethane	>99.98	>99.98	>99.988	>99.98	>99.98	>99.98
Methylene chloride	99.9998	99.9996	99.9996	99.9998	>99.9998	>99.9997
Chloroform	99.9996	99.998	99.9993	99.998	>99.9993	99.999
Carbon tetrachloride	>99.991	99.98	>99.991	>99.98	>99.98	>99.98
Trichloroethylene	>99.95	>99.8	--	--	--	>99.92
1,1,2-Trichloroethane	>99.93	>99.8	>99.9	>99.8	>99.8	>99.9

TABLE 4-5. REMOVAL EFFICIENCY FROM WATER FOR SECOND TEST DAY (PERCENT)

Compound	Run 2-1	Run 2-2	Run 2-3	Run 2-4	Run 2-5	Run 2-6	Average
Chloromethane	>99.98	>99.98	>99.98	>99.98	>99.98	>99.98	>99.98
Methylene chloride	99.9995	>99.9999	>99.9998	>99.9998	99.9998	99.9992	>99.9997
Chloroform	>99.9996	>99.9994	>99.9996	>99.9995	>99.9996	>99.9996	>99.9996
Carbon tetrachloride	>99.991	>99.98	>99.991	>99.98	>99.98	>99.991	>99.990
Trichloroethylene	>99.90	>99.8	--	--	>99.91	>99.8	>99.8
1,1,2-Trichloroethane	--	--	--	--	>99.8	>99.8	>99.8

TABLE 4-6. RESULTS OF VAPOR ANALYSES

Date	Time	Location	Concentration (volume percent at 1 atm and 25 °C) Chloromethane	Methylene chloride	Chloroform	Carbon tetrachloride
9-24-86	10:54	Primary condenser vent (S8)	0.62	37.8	3.87	0.18
9-24-86	12:32		0.63	39.2	3.99	0.19
9-24-86	12:34		0.62	38.7	3.88	0.17
9-24-86	12:37		0.63	38.8	3.91	0.18
9-24-86	14:45		0.59	40.1	4.39	0.20
9-25-86	08:50		0.48	40.0	4.42	0.24
9-25-86	11:10		0.50	38.4	4.36	0.27
9-25-86	12:09		0.48	40.4	4.47	0.25
9-24-86	10:40	Secondary condenser vent (S9)	0.59	40.2	4.60	0.23
9-24-86	12:54		0.59	38.2	4.41	0.57
9-24-86	12:56		0.58	38.5	4.13	0.32
9-24-86	12:58		0.46	31.6	3.21	0.21
9-24-86	14:59		0.59	40.0	4.28	0.22
9-25-86	09:08		0.49	39.1	4.43	0.23
9-25-86	10:40		0.48	39.9	4.47	0.24
9-25-86	11:49		0.47	41.2	4.71	0.26
9-24-86	11:10	Storage tank vent (S10)	0.019	1.20	0.31	0.087
9-24-86	13:18		0.19	9.83	2.47	0.71
9-24-86	15:33		0.19	9.69	2.53	0.75
9-25-86	09:43		0.20	12.0	3.12	0.79
9-25-86	11:21		0.19	11.9	3.12	0.79
9-25-86	12:20		0.19	11.8	3.08	0.78
9-24-86	11:05	Organics collection tank (S11)	0.0073	2.44	0.47	0.020
9-24-86	15:27		0.0029	1.17	0.23	0.044
9-24-86	10:47	Solids decanter vent (S12)	1.04	27.7	7.11	2.53
9-24-86	15:10		0.70	25.9	7.04	3.00
9-25-86	09:34		0.57	32.2	6.43	1.54

TABLE 4-7. COMPARISON OF VAPOR CONCENTRATIONS AT PRIMARY (S8) AND SECONDARY (S9) CONDENSER VENTS (VOLUME PERCENT)

Compound	Concentration at S8	Concentration at S9	RPD[a]
Chloromethane	0.568	0.530	6.9
Methylene chloride	39.2	38.6	1.5
Chloroform	4.16	4.28	2.8
Carbon tetrachloride	0.210	0.286	31
Total VO	44.1	43.7	1.0

[a]RPD = relative percent difference.

not significantly different for the major components, considering the precision of sampling and analysis. The relative percent difference is only 1.5 percent for the major component (methylene chloride) and 2.8 percent for chloroform. The difference between total VO concentrations was only 1 percent.

The vapor flow rate at S8 was measured by diverting the vapor flow to the atmosphere at the condenser through a dry test meter. The measured flow rates are listed in Table 4-8 and reveal an average of about 57 L/min. These flow rates are representative of a primary condenser vented directly to the atmosphere. However, the vapors from the primary condenser travel through piping to the secondary vent condenser. Consequently, the steam stripper is operated at a backpressure of about 1.5 pounds per square inch gauge (psig) at the primary condenser, which increases condensation and decreases the flow rate during normal operation. Vapor flow rates measured at the secondary condenser (S9) are given in Table 4-9. The flow rate at this point ranged from 11 to 13.6 L/min and was measured with a wet test meter. The difference in measured flow rates at S8 and S9 can be accounted for partially by the change in backpressure and in the flow route. However, the difference in flow rates also may have been caused by undetected leaks in the vent system used for the secondary condenser. Figure 4-1 shows that the two solids decanters also are vented to the secondary condenser. Any leaks around these decanter tops or vents or leaks in the overhead piping may have resulted in lower measured flows at the secondary condenser (S9). Both test meters had been carefully calibrated with a standard wet test meter. Consequently, the meter calibration should not have contributed to any differences between the two measured flow rates.

The mass flow rates into and from the primary condenser are given in Table 4-10. The flow rate of organic compounds into the primary condenser were calculated from the average mass rate entering with the stripper feed water minus the average rate leaving with the stripper bottoms, which was essentially negligible in comparison to the feed rate. The mass rate of compounds leaving with the vapor were calculated from the measured flow rates and concentrations. The condenser efficiency was on the order of 89 to 94 percent for individual compounds with an overall efficiency of 91 percent for total VO. Theoretical calculations indicated that the dew point of the vapors leaving the primary condenser was 21 °C. (The dew point is the temperature at which drops of liquid begin to form from the vapor.) The dew point corresponds approximately to the cooling water temperature and ambient temperature during the 2-day test. The removal efficiency predicted for the condenser was estimated from vapor-liquid equilibrium data, with the results listed in Table 4-11. The predicted efficiencies agree well with the measured efficiencies for the two major compounds, methylene chloride and chloroform. The agreement was poorer for carbon tetrachloride and chloromethane. Chloromethane is a very volatile compound and is subject to loss during sampling, transport, and analysis. If the actual feed concentrations of chloromethane were higher than the reported values because of low recovery, then the measured efficiency would be lower and closer to the predicted efficiency.

The concentrations measured at S8 and S9 and dew point calculations indicate that the secondary condenser was not removing VO from the vapor vented from the primary condenser. Table 4-7 showed no significant difference

TABLE 4-8. VAPOR FLOWRATE FROM PRIMARY CONDENSER (S8)

Date	Time[a]	Flowrate (L/min)[b]
9-24-86	9:31	55.8
	12:03	55.8
	16:03	59.5
	Average	57.0
9-25-86	10:00	54.9
	11:25	56.6
	12:26	58.1
	Average	56.5

[a]Measurements were taken over a 6- to 12-min period.
[b]Corrected to standard conditions.

TABLE 4-9. FLOWRATE MEASUREMENTS FROM SECONDARY CONDENSER VENT (S9)

Date	Time[a]	Flowrate (L/min)[b]
9-24-86	9:07	11.0
	11:44	13.5
	15:53	13.6
	Average	12.7
9-25-86	9:27	11.3
	10:55	11.1
	12:04	11.2
	Average	11.2

[a]Measurements were taken over an 8- to 10-min period.
[b]Corrected to standard conditions.

TABLE 4-10. MASS FLOWRATES INTO AND FROM THE PRIMARY CONDENSER (S8) AND CONDENSER EFFICIENCY

Compound	Flowrates (g/h)			Efficiency (percent)
	Vapor in[a]	Liquid out[b]	Vapor out	
Water	1.16×10^5	1.16×10^5	13	99.99
Chloromethane	75.7	67.1	8.6	88.6
Methylene chloride	1.05×10^4	9.42×10^3	1,050	90.0
Chloroform	2.94×10^3	2.78×10^3	160	94.4
Carbon tetrachloride	136	122	14	89.6
Total VO	1.37×10^4	1.24×10^4	1,230	90.9

[a]From mass balance around stripper.

[b]By difference between inlet and outlet vapor flows.

TABLE 4-11. COMPARISON OF MEASURED AND PREDICTED EFFICIENCIES FOR PRIMARY CONDENSER (S8)

Compound	Efficiency (percent)	
	Predicted	Measured
Chloromethane	49.4	88.6
Methylene chloride	91.0	90.0
Chloroform	95.8	94.4
Carbon tetrachloride	97.5	89.6

between the concentrations measured at S8 and S9. If material had condensed at S9, the vapor samples from S9 would have had a higher concentration of noncondensibles and reduced concentrations of the less volatile compounds. The calculated dew point for both locations was approximately 21 °C, which was roughly equal to the cooling water temperature. The lowest cooling water temperature recorded was 17 °C; consequently, the maximum driving force for heat transfer was 4 °C (21-17). Dew point calculations indicate that reducing vapor temperatures to 17 °C does not increase condensation significantly.

During the test, the secondary condenser did not provide any significant improvement in overall condenser efficiency and recovery of VO. However, the cooling water temperature during the winter months will be lower than during this test. The efficiency of both the primary and secondary vent condensers should improve during the winter months with lower cooling water temperatures. The plant currently is considering the replacement of the vent condenser that uses cooling tower water with one that uses refrigerated glycol. If refrigerated glycol is used to cool the vapors to 2 °C, the efficiency of the secondary condenser will improve significantly. Predicted efficiencies for cooling to 2 °C reveal levels of 67 percent for methylene chloride and 83 percent for chloroform, the two major compounds. The overall removal of total VO by the secondary condenser would improve from around 0 to 68 percent.

Emissions from the storage tank vent (S10) and the solids decanter (S12) were estimated from the measured concentrations of VO in the vapor space. The conservation vent on the storage tank remained closed during the test and probably opens only when material is pumped into the tank. Attempts to measure the vapor flow rate at S12 were not completely successful because the conservation vents on the decanter opened as the decanter was being filled. Sampling modifications had been made to the vent lines, which increased the normal backpressure on the tanks. Consequently, a portion of the vent flow escaped through the conservation vent and was not measured. However, the vapor flow rate from these tanks should equal the volumetric rate at which liquid is displacing the vapor. The emission estimates for these tanks are provided in Tables 4-12 and 4-13. The estimates are based on the measured vapor-phase concentrations and the quantity of water treated for operation during 50 weeks of the year. If the system is operated only 75 percent of the time, the estimates in Tables 4-12 and 4-13 would be commensurately lower. The estimated emissions include only working losses, which are the primary emissions from such process storage tanks. Breathing losses may be estimated from API (American Petroleum Institute) storage tank equations; however, these equations require assumptions on temperature changes and are not included. Emission estimates are not included for the small collection tank. The relatively low vapor-phase concentrations at S11 and low working losses from the low rate of condensate generation suggest that those emissions would be low. The theoretical estimate of emissions from this small tank are difficult to derive because there is no information on the rate of mass transfer through the upper layer of sludge and water. Numerous assumptions also would be required on the average driving force concentration for mass transfer, typical windspeed, etc.

A summary of the major air emission sources is given in Table 4-14. The major source is the initial solids decanters followed by the storage tank and

TABLE 4-12. ESTIMATES OF EMISSIONS FROM STORAGE TANK (S10)

Compound	Emissions		
	g/h[a]	Mg/yr[a]	g/L treated[b]
Chloromethane	9.0	0.08	0.004
Methylene chloride	890	7.48	0.356
Chloroform	325	2.73	0.130
Carbon tetrachloride	112	0.94	0.045
Total VO	1,336	11.2	0.535

[a]Based on operation of 50 weeks per year.

[b]Grams per liter of water treated.

TABLE 4-13. ESTIMATES OF EMISSIONS FROM SOLIDS DECANTERS (S12)

Compound	Emissions		
	g/h[a]	Mg/yr[a]	g/L treated[b]
Chloromethane	43.4	0.36	0.017
Methylene chloride	2,709	22.8	1.08
Chloroform	940	7.90	0.376
Carbon tetrachloride	449	3.78	0.180
Total VO	4,142	34.8	1.658

[a]Based on operation of 50 weeks per year.

[b]Grams per liter of water treated.

TABLE 4-14. SUMMARY OF VAPOR EMISSIONS

Compound	Emissions (g/L treated)			
	Steam stripper	Solids decanters	Storage tank	Total
Chloromethane	0.0034	0.0174	0.0036	0.024
Methylene chloride	0.420	1.084	0.356	1.86
Chloroform	0.0655	0.376	0.130	0.572
Carbon tetrachloride	0.0056	0.180	0.0446	0.230
Total VO	0.494	1.66	0.535	2.69

the overhead system for the steam stripper. The results in Table 4-14 are expressed in terms of grams of emissions per liter of water treated, which is independent of the time of operation. These results suggest that 2.7 g/L of VO in the wastewater eventually may be transferred to the air. Based on dew point calculations, these emissions can be reduced to about 1.1 g/L if the vent condenser is cooled with refrigerated glycol at about 2 °C. The modified condenser would reduce emissions from the solids decanter, storage tank, and the steam stripper's overhead system.

RESULTS FOR PLANT H

Process Description for Plant H

Plant H produces 1,2-dichloroethane (ethylene dichloride or EDC) and vinyl chloride monomer. The following process description is taken from Reigel's Handbook of Industrial Chemicals.[2]

EDC is produced from the chlorination of ethylene, and about 87 percent of the nationwide production of EDC is used in the manufacture of vinyl chloride monomer. The vinyl chloride is used in the manufacture of polyvinyl chloride (PVC) polymer.

EDC is produced at this plant by the oxychlorination reaction shown below:

$$C_2H_4 + 2HCl + 1/2\ O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

The oxychlorination reaction is carried out in a fluid bed of copper chloride-impregnated catalyst. Purified EDC from this process is cracked in a furnace at temperatures of about 400 °C and elevated pressures. The hot gases are quenched and distilled to remove HCl and then the vinyl chloride. HCl is returned to the EDC reactor, and unconverted EDC is returned to the EDC purification process.

Wastewaters from the EDC/VCM production operation and from other parts of the plant, including storm water runoff, are treated in the steam stripper shown schematically in Figure 4-2. Miscellaneous plant wastewater is collected in an equalization tank with a retention time of roughly 24 hours. The separate, continuous wastewater stream from the process is added to the feed line from the equalization tank, and the two combined streams represent the feed to the stripper. The wastewater from the equalization tank is passed through a heat exchanger to provide preheating of the stripper feed. Heat to the heat exchanger is provided by the stripper effluent. The feed rate to the stripper is in the range of 760 to 950 L/min (200 to 250 gal/min).

The feed stream enters the stripper at the top of the column and steam at 50 psig is injected countercurrently at the bottom of the stripping column. Trays (instead of packing) are used inside the column to promote liquid/vapor contact. Overhead vapors from the column pass through a condenser cooled with cooling tower water. Condensate is collected in a decanter/receiver vessel. Vapors not condensed in the first condenser pass through a second condenser cooled with refrigerated glycol. Condensate from this condenser is also collected in the decanter/receiver vessel. Noncondensibles that pass through

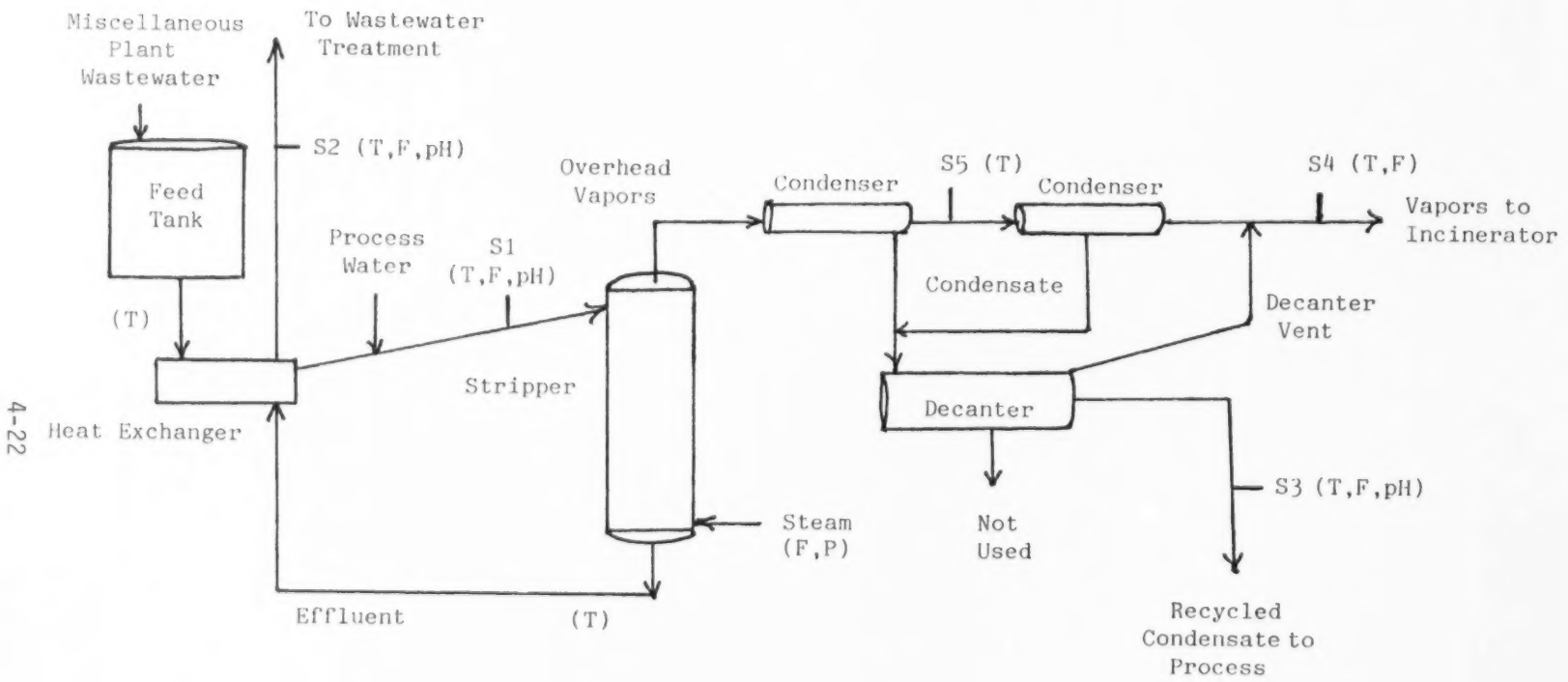

Figure 4-2. Schematic of steam stripper and sampling locations.
(S = sampling point, T = temperature, P = pressure, F = flowrate)

both condensers are collected and vented to an incinerator. The column is maintained at about 4 psig; consequently, the vapor streams described above are maintained at a positive pressure.

The receiving vessel for condensate was previously operated as a decanter. However, both the organic layer and aqueous condensate are currently recycled to the process. This current method of operation does not use the vessel as the decanter. When the vessel is filled to an upper limit switch, the condensate pump comes on, lowers the level to a lower limit switch, and shuts off. The pump cycles on and off depending upon the rate at which condensate is collected. The effluent from the steam stripper first passes through a heat exchanger to obtain some cooling and to preheat the stripper feed stream. Additional cooling of the effluent is provided in a second heat exchanger (not shown in Figure 4-2) prior to sending it to the wastewater treatment system.

Details on the design of the steam stripper were classified as confidential business information and are not included in this report.

Removal of VO From Water

Samples of the stripper feed and bottoms (water leaving the bottom of the steam stripper) were taken for analysis of volatile organics and extractable organics. The analysis of the pretest survey samples indicated that the overwhelming majority of organic compounds in the wastewater were volatile organics. The only extractable organic found was hexachlorobenzene with a concentration of 0.8 ppm entering the stripper and 0.12 ppm leaving with the bottoms. During the test, samples were taken for analysis of extractable organics but only one sample was analyzed initially. This sample confirmed the presurvey results that hexachlorobenzene was the only extractable organic present and revealed a level of 0.044 ppm entering the stripper and less than 0.01 ppm leaving with the bottoms. Because of the high expense of analysis for extractable organics relative to the minimal amount of information obtained (i.e., no significant levels of extractable organics), the other extractable organic samples were not analyzed.

The results for volatile organics analysis are presented in Tables 4-15 and 4-16 and show that 14 constituents were identified and quantified. The results are numbered as Run 1 (first day) and Run 2 (second day) followed by Numbers 1 through 5 to identify the sequence in which they were taken during the day. The results in Tables 4-15 and 4-16 show that 1,2-dichloroethane and chloroform are the major components. The results for 1,2-dichloroethane show a 4 to 5 order-of-magnitude reduction in concentration after the wastewater is steam stripped. The chloroform results are quite variable and show very high reductions for most of the first day of the test and smaller reductions for the second day of the test. The other 12 constituents were present at levels of roughly 1 to 20 ppm in the feed, and all were consistently reduced to below detection limits (0.01 ppm) in the stripper bottoms.

The total VO concentration in the feed over the test averaged approximately 6,000 ppm (0.6 percent) with a range of 4,400 to 8,200 ppm. The total VO concentration in the stripper bottoms was essentially determined by the amount of chloroform remaining in the wastewater. The overall average VO

TABLE 4-15. STRIPPER FEED (IN) AND BOTTOMS (OUT) CONCENTRATIONS FOR FIRST TEST DAY (ppm)

Compound	1-1		1-2		1-3		1-4		1-5	
	In	Out	In	Out	In	Out	In	Out	In	Out
1,2-Dichloroethane	7,100	.06	7,600	.25	6,200	.14	4,600	.20	5,100	.11
Chloroform	370	29	440	.13	220	.20	240	.60	310	.63
Benzene	.32	<.01	.36	<.01	.26	<.01	<.20	<.01	<.50	<.01
Carbon tetrachloride	6.1	<.01	<.20	<.01	2.9	<.01	1.8	<.01	1.5	<.01
Chlorobenzene	.64	<.01	.56	<.01	.50	<.01	.25	<.01	<.50	<.01
Chloroethane	17	<.01	26	<.01	8.8	<.01	5.3	<.01	6.4	<.01
1,1-Dichloroethane	18	<.01	20	<.01	9.8	<.01	7.8	<.01	8.6	<.01
1,1-Dichloroethene	11	<.01	16	<.01	2.5	<.01	2.1	<.01	2.4	<.01
1,2-Dichloroethene	18	<.01	20	<.01	7.1	<.01	5.2	<.01	6.2	<.01
Methylene chloride	1.5	<.01	1.6	<.01	1.0	<.01	1.3	<.01	.80	<.01
Tetrachloroethene	4.8	<.01	4.4	<.01	1.3	<.01	.75	<.01	.70	<.01
1,1,2-Trichloroethane	15	<.01	14	<.01	6.2	<.01	6.0	<.01	3.9	<.01
Trichloroethene	12	<.01	13	<.01	5.1	<.01	2.9	<.01	2.8	<.01
Vinyl chloride	11	<.01	24	<.01	6.9	<.01	7.0	<.01	6.5	<.01

TABLE 4-16 STRIPPER FEED (IN) AND BOTTOMS (OUT) CONCENTRATIONS FOR SECOND TEST DAY (ppm)

	2-1		2-2		2-3		2-4		2-5	
Compound	In	Out	In	Out	In	Out	In	Out	In	Out
1,2-Dichloroethane	4,600	.07	5,900	.034	5,500	.017	4,200	.042	5,500	.043
Chloroform	180	.41	290	11	240	16	160	2.0	260	36
Benzene	<.20	<.01	.22	<.01	.22	<.01	<.20	<.01	<.20	<.01
Carbon tetrachloride	.82	<.01	1.1	<.01	1.1	<.01	<.20	<.01	1.0	<.01
Chlorobenzene	.36	<.01	.30	<.01	.30	<.01	<.20	<.01	<.20	<.01
Chloroethane	7.0	<.01	7.6	<.01	6.7	<.01	4.6	<.01	6.6	<.01
1,1-Dichloroethane	13	<.01	9.3	<.01	8.8	<.01	5.5	<.01	7.3	<.01
1,1-Dichloroethene	3.0	<.01	2.9	<.01	2.5	<.01	1.4	<.01	2.7	<.01
1,2-Dichloroethene	7.2	<.01	7.6	<.01	6.8	<.01	4.7	<.01	6.5	<.01
Methylene chloride	.98	<.01	1.1	<.01	1.1	<.01	.86	<.01	1.8	<.01
Tetrachloroethene	.74	<.01	.44	<.01	.42	<.01	.20	<.01	.40	<.01
1,1,2-Trichloroethane	5.5	<.01	7.2	<.01	5.4	<.01	6.0	<.01	5.7	<.01
Trichloroethene	2.8	<.01	2.9	<.01	2.6	<.01	1.4	<.01	2.2	<.01
Vinyl chloride	5.2	<.01	6.2	<.01	5.7	<.01	4.3	<.01	6.7	<.01

concentration leaving the stripper was 9.7 ppm with a range of 0.34 to 36 ppm. However, the VO concentration in the bottoms for 6 of the 10 runs averaged 0.8 ppm and showed that the stripper was capable of a 4 order-of-magnitude reduction in total VO concentration. The swings in chloroform concentration are consistent with the plant's data, which showed occasionally high levels of chloroform.

The removal efficiencies from water are given in Tables 4-17 and 4-18. The removal of the major component (1,2-dichloroethane) consistently exceeded 99.99 percent and was generally on the order of 99.999 percent. The removal of all other constituents except chloroform was greater than 95 percent and in many cases exceeded 99.9 percent. Only 1,2-dichloroethane and chloroform were detected in the bottoms; consequently, the removal of the other 12 components is based on the detection limits of these compounds in the bottoms stream. The removal efficiency for total VO was essentially determined by the amount of 1,2-dichloroethane and chloroform in the influent and the amount of chloroform in the effluent. An average VO concentration of 6,000 ppm in the influent was reduced to an average of 9.7 ppm in the effluent and represents a removal efficiency of approximately 99.8 percent for total VO.

The removal of chloroform averaged 99.6 percent for 6 of the 10 runs and averaged only 92.4 percent for the other 4 runs. The process data were examined closely, and no positive correlation could be made between chloroform removal and the steam rate, feed temperature, condensate rate, feed concentration of chloroform, pH variation, or the feed rate. However, the removal efficiency for chloroform does appear to be related to fouling of the trays in the column. For example, Table 4-19 shows that the system was backflushed between the samples taken for runs 1-1 and 1-2. After backflushing, the removal of chloroform markedly improved for the balance of the first test day. Chloroform removal deteriorated again during the second test day. At about 13:00, the condensate showed the presence of solids and indicated that the steam stripper's overhead system had been flooded with liquid. This observation was confirmed by a sharp increase in the reported flow rate of condensate. Flooding can be caused by excessive liquid holdup due to tray fouling, and the flooding could also provide some unintentional backflushing of the trays. Note that after the flooding was controlled, the sample taken for Run 2-4 at 13:30 shows a temporary drop in chloroform concentration. During the second test day, the column pressure drop increased slightly and plant personnel stated that they intended to shut the column down for cleaning.

The observations given above suggest that the chloroform removal efficiency is probably affected by tray fouling. However, column fouling can be experienced by any steam stripping operation and periodic cleaning is required. Subsequent conversations with a representative of EPA's Office of Water indicated that chloral (C_2HCl_3O, trichloroacetaldehyde) is formed in the production process and can decompose in the column to form chloroform. Removal efficiency for chloroform is supposedly increased under these conditions if the pH is maintained consistently above 11.[3]

The headspace measurements in Table 4-20 show the effect of high and lower removal efficiencies of chloroform on potential air emissions from the stripper bottoms. The feed to the stripper for the two samples have VO

TABLE 4-17. REMOVAL EFFICIENCIES FROM WATER FOR FIRST TEST DAY (PERCENT)

Compound	1-1	1-2	1-3	1-4	1-5	Average
1,2-Dichloroethane	99.9991	99.998	99.998	99.995	99.998	99.998
Chloroform	91.7	99.98	99.8	99.7	99.8	98.2
Benzene	>96.7	>98.1	>96.5	---	---	>97.1
Carbon tetrachloride	>99.8	---	>99.7	>99.4	>99.3	>99.6
Chlorobenzene	>98.4	>98.8	>98.2	>95.7	---	>97.8
Chloroethane	>99.94	>99.98	>99.90	>99.8	>99.8	>99.9
1,1-Dichloroethane	>99.94	>99.97	>99.91	>99.86	>99.88	>99.9
1,1-Dichloroethene	>99.91	>99.96	>99.6	>99.5	>99.6	>99.7
1,2-Dichloroethene	>99.94	>99.97	>99.87	>99.8	>99.8	>99.9
Methylene chloride	>99.3	>99.96	>99.1	>99.2	>98.6	>99.2
Tetrachloroethene	>99.8	>99.85	>99.3	>98.5	>98.5	>99.2
1,1,2-Trichloroethane	>59.93	>99.95	>99.85	>99.8	>99.7	>99.8
Trichloroethene	>99.91	>99.95	>99.8	>99.6	>99.6	>99.8
Vinyl chloride	>99.91	>99.97	>99.86	>99.85	>99.84	>99.9

TABLE 4-18 REMOVAL EFFICIENCIES FROM WATER FOR SECOND TEST DAY (PERCENT)

Compound	2-1	2-2	2-3	2-4	2-5	Average
1,2-Dichloroethane	99.998	99.9994	99.9997	99.9990	99.9993	99.9991
Chloroform	99.8	96.3	93.2	98.5	88.4	95.2
Benzene	---	>95.5	>95.5	---	---	>95.5
Carbon tetrachloride	>98.8	>99.1	>99.1	---	>99.2	>99.1
Chlorobenzene	>97.1	>96.6	>96.7	---	---	>96.8
Chloroethane	>99.85	>99.86	>99.85	>99.7	>99.87	>99.8
1,1-Dichloroethane	>99.92	>99.89	>99.89	>99.78	>99.88	>99.87
1,1-Dichloroethene	>99.7	>99.7	>99.6	>99.1	>99.7	>99.6
1,2-Dichloroethene	>99.85	>99.86	>99.86	>99.7	>99.87	>99.8
Methylene chloride	>98.9	>99.1	>99.1	>98.6	>99.5	>99.0
Tetrachloroethene	>98.6	>97.7	>97.7	>93.9	>97.9	>97.2
1,1,2-Trichloroethane	>99.80	>99.86	>99.82	>99.80	>99.85	>99.8
Trichloroethene	>99.6	>99.7	>99.6	>99.1	>99.6	>99.5
Vinyl chloride	>99.8	>99.8	>99.8	>99.7	>99.9	>99.8

TABLE 4-19. RESULTS FOR CHLOROFORM

Time	Run Number	Chloroform Concentration (ppm) In	Chloroform Concentration (ppm) Out	Removal Efficiency (%)	Comments
7:20	1-1	370	29	91.7	The system was backflushed around 9:00.
9:20	1-2	440	0.13	99.98	
11:20	1-3	220	0.20	99.8	Operation normal per plant.
14:00	1-4	240	0.60	99.7	Operation normal per plant.
15:30	1-5	310	0.63	99.8	Operation normal per plant.
8:00	2-1	180	0.41	99.8	a
9:30	2-2	290	11	96.3	a
11:30	2-3	240	16	93.2	a
13:30	2-4	160	2.0	98.5	The overhead system flooded at 13:00.
15:30	2-5	260	36	88.4	a

[a]During the second test day, the pressure drop across the column appeared to increase slightly throughout the day and suggests column fouling problems. The plant planned to shut the steam stripper down upon completion of our test to "hydroblast" (high pressure water cleaning) the column and trays.

TABLE 4-20. HEADSPACE RESULTS FOR FEED AND BOTTOMS (mg/L at 25 °C)

Constituent	Headspace Concentration of Feed		Headspace Concentration of Bottoms	
	Day 1[a]	Day 2[b]	Day 1[c]	Day 1[d]
1,2-Dichloroethane	120	34	<0.05	<0.05
Chloroform	12	12	2.5	<0.05
Benzene	<0.05	<0.05	<0.05	<0.05
Carbon tetrachloride	5.3	.26	<0.05	<0.05
Chlorobenzene	.072	<0.05	<0.05	<0.05
Chloroethane	3.9	.88	<0.05	<0.05
1,1-Dichloroethane	3.3	.99	<0.05	<0.05
1,1-Dichloroethene	3.5	.46	<0.05	<0.05
1,2-Dichloroethene	3.0	.72	<0.05	<0.05
Methylene chloride	.08	.11	<0.05	<0.05
Tetrachloroethene	1.1	.06	<0.05	<0.05
1,1,2-Trichloroethane	.77	.18	<0.05	<0.05
Trichloroethene	3.2	.27	<0.05	<0.05
Vinyl chloride	3.4	1.3	<0.05	<0.05
Totals	160	51	<3.2	<0.7

[a]Corresponding in time to Run 1-1.

[b]Corresponding in time to Run 2-3.

[c]Corresponding in time to Run 1-1 when the chloroform concentration in the bottoms was 29 ppm.

[d]Corresponding in time to Run 1-2 when the chloroform concentration in the bottoms was .13 ppm.

concentrations in the vapor that ranged from 51 to 160 mg/L. When the chloroform removal efficiency was 99.98 percent (Run 1-2), none of the compounds were detected in the vapor phase of the stripper bottoms at a detection limit of 0.05 mg/L. For Run 1-1, the chloroform concentration in the bottoms was 29 ppm (removal efficiency of 91.7 percent) and the only compound detected in the vapor phase was chloroform at 2.5 mg/L. Both samples of bottoms show a significant reduction in headspace concentration; however, when the stripper was performing well, none of the volatile compounds were detected in the headspace of the stripper bottoms.

Condenser Efficiency

Condenser efficiency was evaluated from the organic loading (organics entering the condenser with the vapor) and the quantity of organics leaving through the condenser vent. The difference between the mass rates of organics entering with the feed and the mass rates of organics leaving the stripper with the bottoms represents the organic loading on the condenser. These mass rates are summarized in Table 4-21 for all constituents that were detected in the vented vapor. The 1,2-dichloroethane was by far the major organic constituent entering the condenser.

The mass rate of organics leaving the condenser vent were determined from the measurement of the vent flow rate and concentration. The mass rates leaving the condenser vent are summarized in Table 4-22. The condenser efficiency for the major component (1,2-dichloroethane) was consistently above 99 percent. However, as the vapor phase concentration decreases and the volatility of individual constituents increases, the condenser efficiency drops. Solubility of the vapor constituents in the condensate may also affect condenser efficiency. The overall mass rates out of the condenser vent average about 20 Mg/yr of VO for this system. In this installation, these vented VO are destroyed in an incinerator. However, the results suggest that similar steam strippers with the condenser vented to the atmosphere could have air emissions of 12 to 51 Mg/yr. These rates represent emissions from the secondary condenser cooled with glycol at about 2 °C. The emission rates would be expected to be higher for condensers cooled only with cooling tower water at ambient temperatures (e.g., 29 °C).

The overall condenser efficiency for total VO is high because the removal is dominated by the high loading of a single constituent (1,2-dichloroethane). An average VO loading of 68 g/s is reduced to an average vent rate of 0.63 g/s and represents a VO control efficiency of 99.1 percent.

Process Costs and Limitations

The company supplied cost information for the steam stripping operation to permit an evaluation of cost effectiveness. The basic equipment includes the feed storage tank and surge tank, heat exchanger, the column and trays, two condensers in series (one for cooling tower water followed by a refrigerated glycol condenser), decanter, 8 pumps (4 @ 25 Hp, 2 @ 40 Hp, 2 @ 7.5 Hp), instrumentation (see Table 4-23), piping, and insulation. The installed capital cost in 1986 dollars provided by the company is $950,000. The major annual operating cost components are listed in Table 4-24 and include utilities

TABLE 4-21. ORGANIC LOADING ON THE CONDENSER[a]
(g/s)

Compound	Run 1-1V	Run 1-2V	Run 1-3V	Run 2-1V	Run 2-2V	Run 2-3V
Vinyl chloride	.18	0.10	.092	.075	.050	.079
Chloroethane	.20	0.10	.091	.10	.054	.078
1,1-Dichloroethene	.12	0.034	.034	.043	.016	.032
1,1-Dichloroethane	.15	.13	.12	.19	.064	.086
1,2-Dichloroethene	.15	.091	.088	.10	.055	.032
Chloroform	3.3	3.3	4.4	2.6	1.9	2.7
1,2-Dichloroethane	57	79	72	66	49	65
Totals	61	83	77	69	51	68

[a]Determined by the difference in mass rates entering the stripper with the feed and leaving with the effluent. Averaged over time intervals that correspond approximately to the time that the vapor samples were taken.

TABLE 4-22. CONDENSER VENT RATES (g/s) AND CONDENSER REMOVAL EFFICIENCY (percent)[a]

Compound	Run 1-3V		Run 2-1V		Run 2-2V		Run 2-3V		Average		Range
	Rate	Efficiency	Rate	Efficiency	Rate	Efficiency	Rate	Efficiency	Rate	Efficiency	
Vinyl chloride	.078	15	.12	0	.065	0	.072	8.9	.084	6	(0-15)
Chloroethane	.032	65	.068	32	.035	35	.036	54	.043	47	(32-65)
1,1-Dichloroethene	.016	53	.058	0	.020	0	.030	6.0	.031	15	(0-53)
1,1-Dichloroethane	.0073	94	.021	89	.011	83	.011	87	.013	88	(83-94)
1,2-Dichloroethene	.0054	94	.017	83	.008	85	.0088	73	.0098	84	(73-94)
Chloroform	.065	98.5	.17	93	.10	95	.10	96	.11	96	(93-99)
1,2-Dichloroethene	.17	99.8	.54	99.2	.40	99.2	.26	99.6	.34	99.5	(99.2-99.8)
Totals (g/s)	.37		.99		0.64		.52		.63		
(Mg/yr)	12		31		20		16		20		

[a]Based on the propane tracer results.

TABLE 4-23. PROCESS INSTRUMENTATION

Steam flow rate
Bottoms level indicator
Column differential pressure
Decanter level indicator
Overhead pressure
Feed pH
Storage tank pH
Feed flow rate
Storage tank level
Surge tank pH and pressure
Column temperatures
Heat exchanger temperatures

TABLE 4-24. COST ESTIMATE FOR THE STEAM STRIPPER

Total installed capital cost (1986 dollars)	$950,000
Annual operating cost	$250,000/yr

Components of annual cost (stated by company to be in 1986 dollars)

Utilities (steam, water, electricity)	$225,000/yr
Operating labor	1,100 h/yr
Maintenance labor	14,000 h/yr
Laboratory support	$ 85,000/yr
Recovery credit for organics[a]	$400,000/yr

Total annualized cost estimate

		$/yr
Annual operating cost		250,000
Capital recovery[b]		155,000
Total annualized cost		405,000
Cost effectiveness	($/ton VO removed)	203
	($/Mg VO removed)	223
Cost effectiveness[c]	($/1,000 gal treated)	3.38
	($/ton treated)	0.81
	($/Mg treated)	0.89

[a]4 million lbs/yr at $0.1/lb.

[b]Capital recovery factor = 0.163 (10 years at 10 percent).

[c]Based on treatment of 1.2×10^8 gal/yr.

(primarily steam), operating and maintenance labor, laboratory support for analyses, and a recovery credit for organics (primarily 1,2-dichloroethane) that is recycled to the production process. The annual operating cost was estimated by the facility as $250,000 per year or about $2.08 per 1,000 gallons of wastewater treated. A total annualized cost of $405,000 was derived from the information supplied by the company based on a 10-year lifetime and an interest rate of 10 percent.

Historical data supplied by the company indicated that about 4 million pounds (1,820 Mg) of organics were recovered from the wastewater annually. The cost-effectiveness for removal from water is about $220 per Mg of organics removed. This steam stripper is operated with solids in the feed with levels over 1 percent for dissolved solids and about 0.1 percent for suspended solids. The major operational problems that are experienced include fouling and plugging of the column's trays and the heat exchanger. The annual downtime is about 350 to 450 hours per year or about 4 to 5 percent of the total utilization time. The major limitation in the steam stripper's operation is the restriction of flow and heat exchange because of fouling from the accumulation of solids. The pH control on the system is also difficult to maintain. The pH of the stripper feed ranged from 4.9 to 8.7 and the pH of the effluent ranged from 5.6 to 9.3. It is not known how the variations in pH affect the stripper's performance. These limitations and other operational problems are probably reflected in the estimate of maintenance labor required annually (14,000 hours).

SECTION 5

FIELD TEST RESULTS: STEAM STRIPPING/CARBON ADSORPTION

SITE AND PROCESS DESCRIPTION FOR PLANT G

Plant G is an explosives manufacturing plant; the wastewater streams that are produced are predominantly water soluble. The two major waste streams are redwater and whitewater. The waste streams pass through decanters where the oils are separated from the aqueous phase. A surface impoundment (lagoon) is used as a large storage vessel to provide a stable flow to the stream stripping unit. The steam stripper removes organic compounds and water from the waste stream. The organics separate and are transferred to an organic slop-sump. The water that separates from the steam stripper condensate is recycled to the wastewater stream.

Figure 5-1 presents a plant layout showing the process flows. Whitewater is discharged from process operations to the whitewater settling tanks where it is transferred to the organic condensate tank. During the tests of the steam stripping column, the discharge from the whitewater organic settling tank was diverted away from the organic settling tank. The aqueous stream (top layer) of the organic condensate tank is transferred to the steam stripping column feed tank. A 7.6-cm (3-inch) overflow from this feed tank is discharged into a lagoon. Waste from the redwater tank is discharged directly into the lagoon.

An 46-cm (18-inch) subsurface pipe transfers the contents of the lagoon into a decanter tank. Other feeds into the decanter tank include a pipe from an organic sump that is supplied with organic bottoms from the feed tank, line water, and pad and walkway runoff. The organic layer from the decanter tank is transferred directly to the organic slop sump. The aqueous overflow from the decanter tank is transferred to the feed tank. When the steam stripping column is run on complete recycle, the discharge from the steam stripping column is directed into the decanter tank, bypassing the carbon adsorption (CA) units. Complete recycle is used for start-up and is not used during normal operation. During normal operation, the effluent from the steam stripper passes through a carbon adsorption unit before discharge.

The steam stripping column treats wastes pumped from the feed tank. The aqueous condensate from the steam stripping vapors separates from the organic condensate in the organic condensate tank and is recycled to the feed tank.

Figure 5-2 presents the flow diagram of the continuous steam stripping unit and carbon adsorber at Plant G. Table 5-1 lists the process streams, their average temperatures, pressures, flow rates, concentrations, and enthalpies. The aqueous waste from the feed tank (F) passes through a heat exchanger, is heated from 27 °C to 83 °C, then fed to the steam stripping

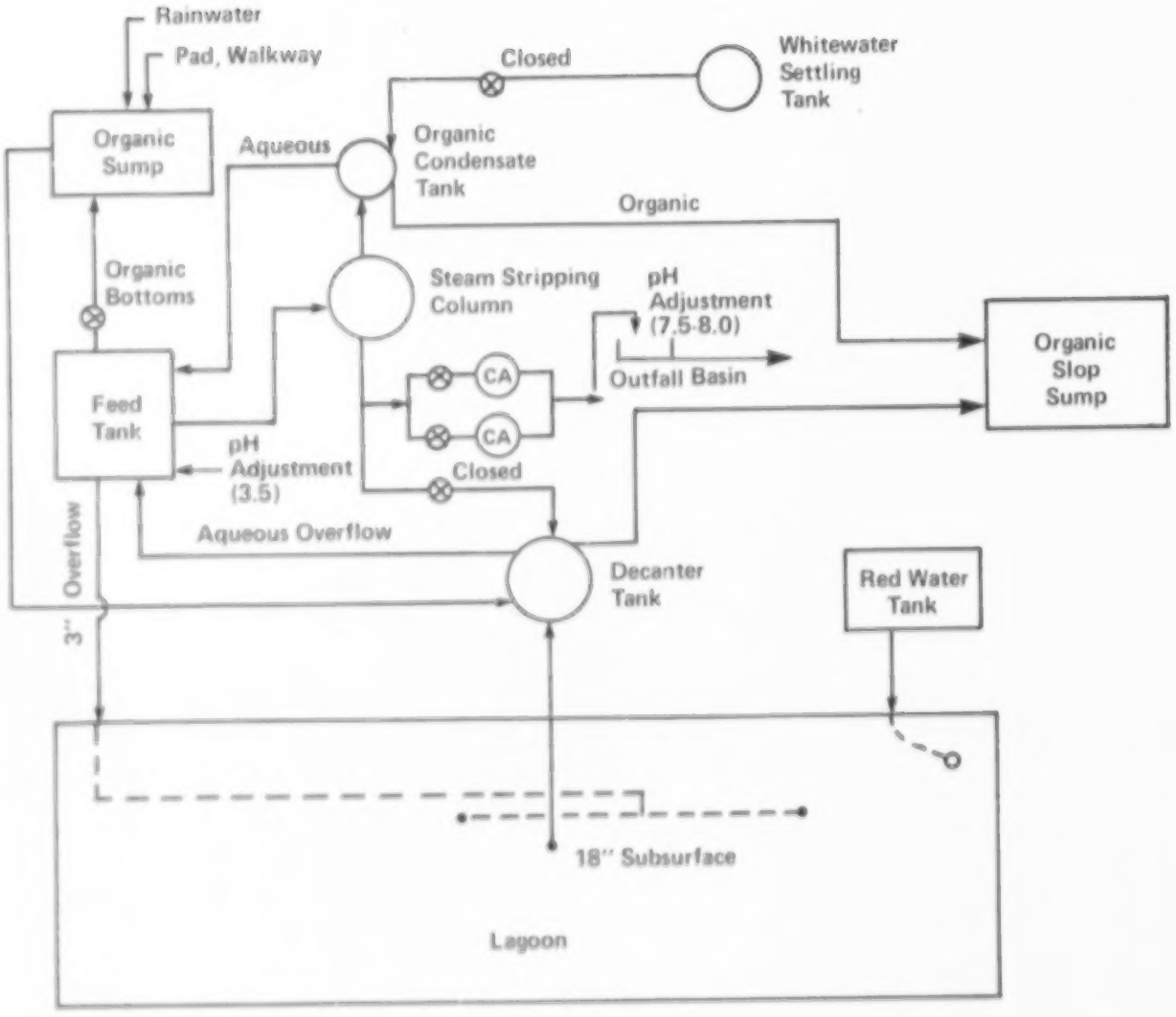

Figure 5-1. Plant layout (not to scale).

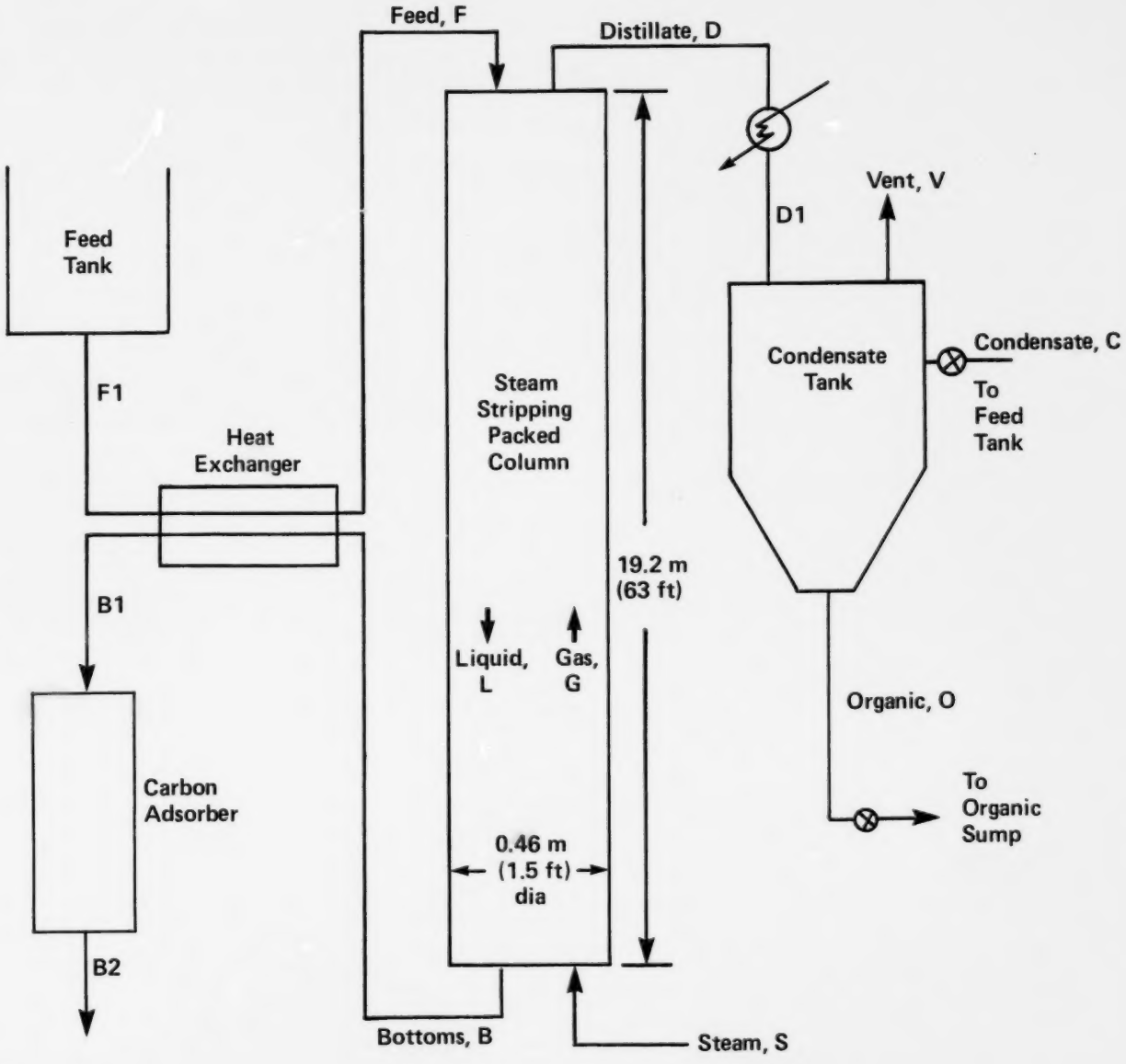

Figure 5-2. Flow diagram of continuous steam stripping and carbon absorption unit.

TABLE 5-1. PROCESS STREAM CHARACTERIZATION

Process stream	Temperature (°C)	Pressure (kPag)	Flow rate (kg/h)	Concentration (mg/kg)[a]			Enthalpy (kJ/kg)
				Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	
F1 Feed before heat ex.	27	NM	29,900[a]	505	78	51	111.7
F Feed after heat ex.	83	NM	29,900[a]	505	78	51	348.3
B Bottoms before heat ex.	112[b]	103	31,490[c]	41	2.4	4.4	468.0[b]
B1 Bottoms after heat ex.	58	NM	31,490[c]	41	2.4	4.4	243.3
B2 Bottoms after carbon adsorption	NM	NM	31,490[c]	<0.8	<0.8	<0.8	--
D Distillate	100	0	443[b]	31,170[d]	5,094[d]	3,129[d]	2,675.6
C Aqueous condensate	NM	NM	427.6[e]	1,900	87	45	--
O Organic condensate	NM	NM	15.4[e]	787,000	193,000	97,000	
V Condensate tank vent	NM	NM	0.34[f]	0[g]	0[g]	0[g]	--
S Steam	128.8	263	2,033	0	0	0	2,709.2

NM = Not measured.
[a]Assumes liquid density = 1.0 kg/L.
[b]From energy balance around column (B, F, D, S).
[c]From mass and energy balance around heat exchanger and column (F1, B1, S, D).
[d]From component mass balance around column (B, F, D, S).
[e]From organic component mass balance around condensate tank (D1, C, O, V).
[f]Very low, assumed zero for calculations.
[g]<0.015 mg/L, gas phase.

packed column. Heat to the heat exchanger is supplied by the treated aqueous waste (B) from the bottom of the packed column. Steam is fed into the bottom of the packed column (S) and flows upward through the packed column, countercurrent to the liquid flow. The vapors (D) leaving the top of the column are condensed and flow into a condensate tank. The aqueous fraction that separates in the condensate tank (C) is transferred back to the feed tank while the organic bottoms (O) are periodically transferred to the organic slop sump.

The steam stripping packed column is 19.2 m (63 ft) high. The column's internal diameter is 0.46 m (1.5 ft) and is packed with 3.17 m^3 (112 ft^3) of 2.5 cm (1-inch) diameter stainless steel rings. The packing is wetted by the liquid and provides additional surface area for gas-liquid contact.

The effluent from the steam stripping column (B) was first passed through the heat exchanger and then through one of two carbon adsorption units. The carbon served as a polishing step removing residual organics from the waste streams. The carbon was used at a replacement rate of 1,362 to 2,043 kg/day (3,000 to 4,500 lb/day). The carbon was returned to the supplier for offsite regeneration.

The carbon bed operated in a pulsed-feed mode. Fresh carbon was placed on top of the bed an average of 1.5 times a day, with approximately 680 kg (1,500 lb) of carbon per charge. The carbon beds were 9.2 m (30 ft) high with 1.7 m (5.5 ft) outage. There were 18.2 to 20.4 Mg (40,000 to 50,000 lb) of carbon in the carbon bed at a typical operating carbon depth of 7.5 m (24.5 ft).

One of the problems reported with the steam stripping column was heat exchanger fouling on the feed preheater. The downtime on the units was reported as less than 1 percent of running time by Plant G personnel. The operating manpower requirements for the continuous steam stripping unit and associated lagoons and tanks were reported as 8 h of manager time, 1/2 h of laboratory time, and 24 h of operator time per day.

The instrument department at Plant G regularly calibrates the flow measuring devices. The steam flow rate was controlled at 127 °C (260 °F) on the bottom. The pressure of the steam is supplied at 25 to 40 psig. The plant can raise the header pressure if necessary to maintain the bottom temperature in the inlet steam. The bottom of the column is maintained at 15 psig. The packed column was operated without any recycle from the condensate directly into the packed column, but there was an indirect recycle of the condensate aqueous phase through the feed tank, which included mixing with other feeds, and then being transferred to the top of the packed column through the heat exchanger.

RESULTS FOR PLANT G

Process Stream Composition

The process streams analyzed were liquid (aqueous and organic) and gaseous. The components measured in the liquid streams were nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene. The only components identified in the vent gas samples were 1,5-hexadiyne ($HC:::CCH_2CH_2C:::CH$) and toluene. The

1,5-hexadiyne was identified using GC/MS. The individual analyses for each stream were averaged, and these averages were used in the process calculations. Table 5-2 lists the average concentrations of each sampled process stream.

Ideally, the flow rates and concentrations of each stream would be measured, and mass and energy balances would be used to check the validity of the data. In this system, flow rates were measured on only three streams, temperatures on four streams, and pressure on one stream. Collection of samples and process data was limited by the availability of flowmeters, thermocouples, pressure transducers, and sampling ports installed in the system. Mass and energy balances were solved for data on streams that were not completely characterized by direct means. Table 5-3 lists the temperatures, pressures, flow rates, concentrations, and enthalpies of the process streams for the steam stripper-carbon adsorber. Table 5-4 shows the results of individual component mass balances around the steam stripper and condensate tank. The measured organics in the liquids are considered semivolatiles because each boils above 200 °C and is only slightly soluble in water. The toluene and 1,5-hexadiyne are both volatiles. Characteristics of the three compounds are listed in Table 5-5.

Removal Efficiencies of the Steam Stripper-Carbon Adsorber

The process consisted of two distinct operations: the steam stripping of the feed waste and the carbon adsorption that follows. Removal efficiencies can be calculated for each of the processes separately and for the combined process. Table 5-6 shows the removal efficiency of the steam stripper, carbon adsorber, the total process for each organic (nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene), and the total organics. The carbon adsorber effluent samples had organic concentrations below the analytical detection limit, so the calculated removal efficiencies involving the carbon adsorber are based on the reported detection limits. Hence, they represent minimum removal efficiencies and would be higher if the true concentrations of the adsorber effluent were actually measured. Steam stripping followed by carbon adsorption effectively treats the feed waste stream. Steam stripping removed 92 percent of the organics fed to the process, and the carbon adsorber further reduced the concentrations below the analytical detection limit ($<$0.8 mg/kg, with $>$95 percent removal in the carbon adsorber).

Process Limitations

The feed to be treated should have relatively little dissolved solids because they will (1) coat the heat exchanger surfaces, (2) clog the column packing, and (3) clog the carbon bed. The feed stream had a total solids content of 23 g/L, and the plant reported heat exchanger fouling as a problem associated with the process (but with downtime of only 1 percent operating time).

Steam requirements could be reduced by using a larger, more efficient heat exchanger between the feed (F1) and bottoms (B) stream. Each 1 °C increase in the feed temperature decreases the steam requirements by 53 kg/h or 2.6 percent of the steam consumption. The capital (purchase cost) and operating

TABLE 5-2. MEASURED CONCENTRATION OF ORGANICS IN PROCESS STREAMS

	Process stream	Sampling point	Average concentration (μg/mL)				
			Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	1,5-Hexadiyne	Toluene
F,F1	Feed	1-VOC	500	78	51	--	--
B,B1	Bottoms	2-VOC	40	2.4	4.4	--	--
B2	Carbon effluent	3-VOC	<0.8	<0.8	<0.8	--	--
Ø	Organic condensate	4-VOC	787,000	193,000	97,000	--	--
C	Aqueous condensate	5-VOC	1,900	87	45	--	--
V	Condensate tank vent	6-VOC	<0.015[a]	<0.015[a]	<0.015[a]	1.4[a]	0.4[a]

[a]Gas concentration.

TABLE 5-3. PROCESS STREAM CHARACTERIZATION

Process stream	Temperature (°C)	Pressure (kPag)	Flow rate (kg/h)	Concentration (mg/kg)[a]			Enthalpy (kJ/kg)
				Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	
F1 Feed before heat ex.	27	NM	29,900[a]	505	78	51	111.7
F Feed after heat ex.	83	NM	29,900[a]	505	78	51	348.3
B Bottoms before heat ex.	112[b]	103	31,490[c]	41	2.4	4.4	468.0[b]
B1 Bottoms after heat ex.	58	NM	31,490[c]	41	2.4	4.4	243.3
B2 Bottoms after carbon adsorption	NM	NM	31,490[c]	<0.8	<0.8	<0.8	--
D Distillate	100	0	443[b]	31,170[d]	5,094[d]	3,129[d]	2,675.6
C Aqueous condensate	NM	NM	427.6[e]	1,900	87	45	--
O Organic condensate	NM	NM	15.4[e]	787,000	193,000	97,000	
V Condensate tank vent	NM	NM	0.34[f]	0[g]	0[g]	0[g]	--
S Steam	128.8	263	2,033	0	0	0	2,709.2

NM = Not measured.
[a]Assumes liquid density = 1.0 kg/L.
[b]From energy balance around column (B, F, D, S).
[c]From mass and energy balance around heat exchanger and column (F1, B1, S, D).
[d]From component mass balance around column (B, F, D, S).
[e]From organic component mass balance around condensate tank (D1, C, O, V).
[f]Very low, assumed zero for calculations.
[g]<0.015 mg/L, gas phase.

Table 5-4. COMPONENT MASS BALANCE AROUND STEAM STRIPPER AND CONDENSATE TANK (STREAMS F, B, C, O, S)

	Flow rate (kg/h)		
	In (S+F)	Out (B+C+O)	% Difference
Nitrobenzene	15.10	14.22	+6.0
2-Nitrotoluene	2.33	3.09	-28.0
4-Nitrotoluene	1.53	1.65	+7.6
Total organics[a]	18.96	18.96	0.0[b]
Water	31,914.04	31,914.04	0.0[b]
Total	31,933	31,933	0.0[b]

[a]Nitrobenzene + 2-nitrotoluene + 4-nitrotoluene.

[b]Redundant calculation; these components are mass balances used in earlier calculations.

TABLE 5-5. CHARACTERISTICS OF MEASURED ORGANICS[a]

	Molecular weight	Melting point (°C)	Boiling point (°C)	Density (g/mL)
Nitrobenzene	123.11	5.7	210.8	1.204
2-Nitrotoluene	137.14	-9.6	221.7	1.163
4-Nitrotoluene	137.14	54.5	238.3	1.104[b]
Toluene	92.15	-95	110.6	0.867
1,5 Hexadiyne	78.12	-6	86	0.8049

[a]From CRC Handbook of Chemistry and Physics, 58th edition.

[b]70° C.

TABLE 5-6. REMOVAL EFFICIENCIES (%)

	Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	Total[b]
Steam stripper	91.5	96.7	90.9	92.1
Carbon adsorber[a]	>98.1	67.1	>82.0	>95.0
Steam stripper and[a] carbon adsorber	>99.8	>98.9	>98.4	>99.6

[a]Effluent concentrations from the carbon adsorber were below quantitation limits. Indicated efficiencies calculated were based on a <0.8-mg/kg detection limit.

[b]Total removal efficiency of nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene.

costs (fouling problems, pressure drop) of the heat exchanger increase with the heat exchanger size, so some optimum (least total cost) sized heat exchanger exists.

The carbon adsorption process produces 1,362 to 2,043 kg (3,000 to 4,500 lb) of spent carbon per day. This carbon contained approximately 31 kg of nitrobenzene, 1.8 kg of 2-nitrotoluene, 3.3 kg of 4-nitrotoluene, and adsorbed solids from the feed stream. Clearly, the regeneration or disposal of the spent carbon is a major process limitation.

PROCESS RESIDUALS

Air Emissions

Air emissions from the steam stripper process were minimal. The condensate tank vent flow rate was too small to be measured reliably with the pitot tube used, and the organic concentrations (measured both onsite and with grab samples) varied widely. The condensate tank vent is a necessary part of the apparatus in that it (1) provides a tank vent when adding or removing liquid from the tank and (2) vents noncondensable components from the condenser. If the vent were not present, noncondensable gases (e.g., air entrained in the feed) would accumulate in the condenser and impair its performance. The condenser vent flow rate, in the absence of liquid level changes in the condensate tank, depends on the amount of noncondensable material entering with the feed.

The vent gas flow was estimated by assuming that the feed wastewater to the stripper was saturated with air and that the air was removed from the water and exited through the condensate tank vent. This flow (0.34 kg/h, or 9.4 L/min) was very small compared to the other system flows, and it corresponds to the maximum possible flow rate through the vent (in the absence of other noncondensable components).

The observed pitot tube pressure drop and measured organic concentrations are compiled in Table 5-7. The maximum vent gas emissions (Table 5-8) were estimated by using the maximum concentrations measured in the vent and the estimated vent flow rate. The actual vent emissions would be considerably lower than this estimate because the average vent gas organic concentration was observed to be much lower than the observed maximums. The average emissions would probably be about one-tenth of the maximum emissions if the observed concentration variation is representative.

The two compounds identified in the vent gas were not detected in any of the liquid samples. The feed concentrations required to produce the maximum observed vent concentration were 0.03 μg/mL for toluene and 0.18 μg/mL for 1,5-hexadiyne. Both concentrations were well below the detection limit for feed organics (0.8 μg/mL); therefore, they would not be detected in the feed wastewater.

TABLE 5-7. VENT GAS MEASUREMENTS, SAMPLE LOCATION 6-VOC[c]

Time	Sample number	P pitot[b] tube (inches $H_2Ø$)	Bacharach TLC (ppm hexane)	Gas concentrations (g/L)				
				Nitrobenzene	2-Nitrotoluene	4-Nitrotoluene	1,5-Hexadiyne	Toluene
12:25	FCC-6-VOC-1	Ø.Ø2	2ØØ-3ØØ	<15	<15	<15	12Ø	77
12:52	FCC-6-VOC-2A	Ø.Ø1	2,ØØØ[a]	<15	<15	<15	5,5ØØ	1,4ØØ
12:56	FCC-6-VOC-2B	Ø.Ø1	NM	<15	<15	<15	57Ø	29Ø
13:5Ø	FCC-6-VOC-3	Ø.Ø4	1,ØØØ-2,ØØØ[a]	<15	<15	<15	56Ø	22Ø
14:45	FCC-6-VOC-4	Ø.Ø1	1Ø-4ØØ[a]	<15	<15	<15	14Ø	8Ø

NM=Not measured.

[a]Highly variable during sampling.

[b] P too low to measure gas flow reliably using pitot tube.

[c]The vent gas flow was irregular and was discharged under high wind conditions (>5ØØ cm/s). The temperature of the vent was approximately ambient.

TABLE 5-8. ESTIMATION OF MAXIMUM CONDENSATE TANK VENT EMISSIONS[a]

Compound	Maximum measured concentration (mg/L)	Estimated maximum emission rate	
		(g/h)	(kg/yr[d])
Toluene[b]	1.4	0.8	6.7
1,5-Hexadiyne[b]	5.5	3.1	26.0
Total hydrocarbons[c]	7.0	4.0	33.6

[a]Assumes feed liquid saturated with air, all air exiting through vent.

[b]Analyzed by GC.

[c]Originally measured as ppm hexane with Bacharach TLC.

[d]Fifty-week, 24-h/day year.

Liquid and Solid Residuals

The treated feed liquid had levels of nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene below the analytical detection limit (<0.8 mg/kg) and could probably be discharged as wastewater after its acidity is neutralized.

The major solid residual from the process is approximately 1,360 to 2,040 kg of spent carbon/day from the carbon adsorber. The plant reported that the carbon is regenerated at another location by the supplier. This carbon would contain approximately 31 kg of nitrobenzene, 1.8 kg of 2-nitrotoluene, 3.3 kg of 4-nitrotoluene, and deposited solids from the feed stream. Suspended solids within the feed stream may also settle as a sludge in the lagoon.

PROCESS COST

Plant operators supplied adequate operating cost data, but did not supply any capital cost information. Several attempts to collect capital cost information from the plant failed. Consequently, the capital cost of the process was estimated and used with the plant-supplied operating costs to determine the total annualized cost of the process.

The manpower requirements for the process were 8 hours of manager time, one-half hour of laboratory time, and 24 hours of operator time per day. The plant supplied manpower costs. Other operating costs supplied by the plant were steam cost ($5.25/1000 lb), carbon ($1,260,000/yr), and spare parts/inventory costs ($72,000/yr). The steam cost includes the capital and operating costs of steam generation. The erection and operation of a steam boiler specifically for the operation of the steam stripper would produce annualized steam costs in the same range as this reported steam cost (approximately $6.00/1000 lb). Because most operating plants have existing installed steam boilers, steam costs are treated as utilities in the operation of processes requiring steam. The manpower costs include labor for removing and replacing carbon in the carbon absorbers. The carbon cost includes the transportation costs of spent and fresh carbon, and the costs of thermal regeneration of the spent carbon. Spent carbon is returned to the supplier for thermal regeneration, and this cost is included with the carbon cost.

The total equipment cost of the process was $872,800 while total capital investment was estimated at $1,885,260. Direct annual costs of operation were $1,700,000. Steam cost was 5.5 percent of the direct annual costs of operation, while carbon costs were 75 percent of the direct annual cost.

The cost effectiveness of the process is $14.13/kg organic removed from the water. This is also $0.0089/kg of water treated. The total annualized cost of the process was $2,240,000.

SECTION 6

PROCESS LIMITATIONS AND COMPARISONS

PROCESS LIMITATIONS FOR THIN-FILM EVAPORATION

The major process limitations to the use of TFEs are that feed and bottoms product must be pumpable and that the feed must not foam excessively during processing. The feed and bottoms can be heated to make pumping easier, but they must be pumpable through positive displacement pumps in order to introduce the feed into the evaporator and to withdraw product. If the feed foams excessively during heating and vaporization of material, the body of the TFE will fill with foam and foam/feed will be carried out of the evaporator and into the entrainment separator and condenser. Foaming also reduces the heat transfer to the material being processed. This is a potential problem in treating DAF wastes, as flocculating agents are frequently added to the water passing through this waste treatment process and appear in the waste sludges.

The condenser and vent gas control systems for the process should be designed specifically for the wastes being treated. Most of the organics in the feed that do not condense at the condenser operating temperature will exit through the condenser vent. As a wide variety of petroleum wastes would be handled by the process, some of the prospective feeds would probably have substantial amounts of uncondensable material.

One potential problem is the relatively rapid wear of feed and bottoms pumps when the process is used with feeds containing suspended solids. This is not actually a limitation of the process, but will affect the frequency of pump replacement and the overall operation and maintenance costs of the process. Feed streams containing suspended solids also require mixing in order to prevent phase separation before the material is fed into the TFE.

PROCESS LIMITATIONS FOR STEAM STRIPPING

The steam stripping results for Plants H and I revealed that steam stripping can generally remove over 99 percent of specific volatile compounds from the wastewater. Total VO removal ranged from 99.8 to 99.999 percent. These volatile compounds are those analyzed by purge-and-trap procedures. The results for Plant G showed that steam stripping could also remove semivolatiles (extractable organics) from wastewater, but a lower removal efficiency was seen (92 percent for total VO). Additional treatment by liquid-phase carbon adsorption improved the efficiency to greater than 99.6 percent. Consequently, steam stripping is expected to remove organic compounds with a relatively wide range of volatility. However, if semivolatiles are present, additional treatment may be needed to decrease the effluent concentration. Liquid-phase carbon adsorption is a demonstrated technique to accomplish this.

At Plant H, purgeable volatile organics were reduced from 6,000 ppm to <9.8 ppm. At Plant I, purgeable volatile organics were reduced from 6,000 ppm to <0.037 ppm. Steam stripping of semivolatiles at Plant G reduced a feed concentration of 634 ppm to 48 ppm. Additional treatment of these semivolatiles by carbon adsorption decreased their concentration to below detection limits (<0.8 ppm).

The solids content of the wastewater may be a limitation in the use of steam stripping. At Plant H, the feed contained 1.4 g/L of solids that was processed through the column. However, this steam stripper requires frequent cleaning and experienced occasionally high levels of chloroform in the bottoms, apparently because of column fouling. At Plant I, solids were removed prior to steam stripping to levels of 0.01 g/L. No significant fouling problems are experienced at Plant I, and the operation consistently obtained ppb levels of organics in the effluent. Consequently, solids removal may be an important step in preparing aqueous wastes for steam stripping. However, the process generates a low volume of sludge that may be a troublesome disposal problem. At Plant I, this sludge was handled offsite and incinerated.

Another limitation of steam stripping aqueous wastes is the presence of a separate phase of organics. Flooding of the column was observed at Plant H when a slug of organic layer entered with the feed. A separate organic phase can cause operational problems with the steam stripper and may yield higher than normal bottoms concentrations. The operation at Plant I included decanting any separate organic phase prior to steam stripping.

These tests indicate that steam stripping may be used for aqueous hazardous wastes that contain strippable organic compounds. The presence of solids or a separate organic layer is the major limitation. However, preliminary treatment for solids or organic phase removal can overcome these limitations and produce a wastewater stream for steam stripping. These preliminary treatment steps add to the total treatment costs and, as discussed earlier in the report, create new sources of air emissions.

COMPARISONS

Plants H and I offer some useful comparisons for wastewater containing fairly volatile compounds. The operation at Plant H treated about 850 L/min compared to 42 L/min at Plant I. Solids were removed at Plant I before steam stripping, and at Plant H, the wastewater received no preliminary treatment. At Plant H, the stripper bottoms were treated in the wastewater treatment plant for removal of solids and biodegradation of organics. At Plant I, no additional treatment (other than occasional pH adjustment) is needed prior to discharge.

The steam usage at these plants and others is compared in Table 6-1. The values of 0.036 to 0.1 kg steam/kg water are well within the recommended design values. A comparison of performance is given in Table 6-2. The steam stripper at Plant I obtained very low effluent levels (average of 33 ppb) compared to the other data.

TABLE 6-1. COMPARISON OF STEAM USAGE RATES

Source	Steam usage (kg/kg water)	Comments	Reference
Plant I	0.1	Total VO reduced from 6,000 ppm to 33 ppb	--
Plant H	0.036	1,2-Dichloroethane reduced from 4,600 to 0.16 ppm	--
Plant K	0.10	1,2-Dichloroethane reduced from 15,000 to 0.037 ppm	4
Ehrenfeld and Bass (design)	0.07-0.24	Design range for steam strippers	5
Shukla (design)	0.1-0.3	Design range for steam strippers.	6
Nathan	0.31	Theoretical design to reduce 1,2-dichloroethane from 8,700 ppm to 9 ppm	7

TABLE 6-2. COMPARISON OF PERFORMANCE

1. Plant I continuous steam stripper

Compound	Concentration (ppm) In	Concentration (ppm) Out	Percent removed
Chloromethane	33	<0.005	>99.98
Methylene chloride	4,490	0.020	>99.999
Chloroform	1,270	0.005	99.999
Carbon tetrachloride	55	<0.005	>99.99
Trichloroethylene	5.6	<0.005	>99.9
1,1,2-Trichloroethane	5.3	<0.005	>99.9
Total VO	5,860	0.033	99.999

2. Olin Chemical continuous steam stripper[8]

Compound	Concentration (ppm) In	Concentration (ppm) Out	Percent removed
Methylene chloride	3,600	0.22	99.99
Chloroform	52	5.3	89
Carbon tetrachloride	1.5	0.09	95
Total VO	3,600	5.6	98

3. Plant H continuous steam stripper

Compound	Concentration (ppm) In	Concentration (ppm) Out	Percent removed
1,2-Dichloroethane	5,630	0.097	99.998
Chloroform	270	9.6	96
Other VO	50	<0.01	>99
Total VO	5,950	9.7	>99.8

(continued)

TABLE 6-2. (continued)

4. Plant B fractional batch distillation (5 percent organics in water)[8]

Compound	Concentration (ppm)		Percent removed
	Initial	Final	
Methyl ethyl ketone	30,000	<10	99.98
2,2-Dimethyl oxirane	6,300	<10	99.9
Methanol	3,500	<10	99.9
Methylene chloride	3,100	<10	99.8
Isopropanol	1,900	<10	99.7
Carbon tetrachloride	1,700	<10	99.7
1,1,1-Trichloroethane	710	530	29
Total VO	49,000	575	99

5. Data from Reference 9 for continuous steam strippers

Stripper	Compound	Concentration (ppm)		Percent removed
		In	Out	
1	Methylene chloride	1,430	<0.015	>99.99
2	Methylene chloride	4.7	<0.002	>99.95
3	Methylene chloride	34	<0.01	>99.97
	Chloroform	4,509	<0.01	>99.99
	1,2-Dichloroethane	9.0	<0.01	>99.99

The cost and performance data from Plant H are compared in Table 6-3 with data obtained from a similar stripper during a 1-day plant visit.[4] One difference between the two types is that the stripper examined in this test used trays for vapor/liquid contact whereas the Plant K operation uses a packed column. The basic feed constituents are similar; however, Plant K has a higher concentration of 1,2-dichloroethane in the feed. The difference in annual operating cost is probably attributable primarily to the higher rate of steam usage at Plant K where approximately 75 percent of the annual operating cost is for steam. Both of these steam strippers achieve similar effluent (or bottoms) concentrations of VO in the range of 1 to 2 ppm. Although the steam usage for Plant K appears to be higher, the steam usage for both plants in terms of VO removed is very similar (6.2 and 6.7 kg steam/kg VO removed). The small difference in cost-effectiveness is probably not significant and can be attributed to the higher feed concentrations observed at Plant K.

A comparison of condenser efficiencies is given in Table 6-4. A higher efficiency was observed at Plant H (99 percent), which used refrigerated glycol at 2 °C, than was observed at Plant I (91 percent), which had a condenser cooled with cooling tower water at 21 °C. The highest efficiency was observed for ethylene dichloride at Plant H because of the high vapor-phase concentration and its relatively low vapor pressure. The lowest efficiency was observed for vinyl chloride, which has a very high vapor pressure and is difficult to condense.

TABLE 6-3. COST COMPARISON

Item	Plant H	Plant K[3]
Capital cost ($)	950,000	700 000
Operating cost ($/yr)	250,000	450,000
Total annualized cost ($/yr)[a]	405,000	564,000
Average feed rate (L/min)	818	680
Steam rate (kg/h @ 50 psig)	1,790	4,090
Feed constituents (ppm)		
1,2-Dichloroethane	5,600	15,000[b]
Chloroform	270	17[b]
Other VO	59	31[b]
Bottoms constituents (ppm)		
1,2-Dichloroethane	0.16	.037[b]
Chloroform	0.8[c]	1.3[b]
Other VO	<0.01	1.4[b]
Steam usage		
kg/kg water	0.036	0.10
kg/kg VO removed	6.2	6.7
Cost-effectiveness		
$/Mg VO removed	220[d]	120[e]

[a]Based on a 10-year lifetime at 10% (Capital recovery factor = 0.163).

[b]Based on a single sample analysis from presurvey trip.

[c]Based on 6 of 10 runs.

[d]Based on company data of 1,820 Mg/yr recovered.

[e]Estimated from single analysis and 329 days/year operation.

TABLE 6-4. SUMMARY OF AVERAGE CONDENSER VENT RATES AND EFFICIENCIES

Plant H

Constituent	Condenser loading (g/s)	Vent rate (g/s)	Condenser efficiency (percent)
Vinyl chloride	0.089	0.084	6
Chloroethane	0.081	0.043	47
1,1-Dichloroethene	0.036	0.031	15
1,1-Dichloroethane	0.11	0.013	88
1,2-Dichloroethene	0.006	0.001	84
Chloroform	2.9	0.11	96
Ethylene dichloride	63	0.34	99.5
Total	66	0.62	99

Plant I

Constituent	Condenser loading (g/s)	Vent rate (g/s)	Condenser efficiency (percent)
Chloromethane	0.021	0.0024	89
Methylene chloride	2.9	0.29	90
Chloroform	0.81	0.045	94
Carbon tetrachloride	0.038	0.0039	90
Total	3.8	0.34	91

SECTION 7

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